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*RESONANT ACOUSTIC AND ELECTRIC OSCILLATIONS RELEASED BY THE RELATIVELY SLOW SPRING BREAK**

By Carl Barus

Department of Physics, Brown University

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1. Apparatus.—My last paper (these Proceedings, **11**, 728) indicated that the period of the break in the primary only incidentally influences the period of the secondary and that therefore a break of variable period is not needed. Though not unexpected, this suggested a variety of experiments of which the following are examples.

A mercury break was first tried and gave good service; but the common spring break with platinum contacts is much simpler in manipulation, usually at hand and the results not inferior. I used a small model induction coil, the primary (7 cm. long, 1.5 cm. in diam.) consisting of about 100 turns of wire on an iron wire core about 1 cm. in diameter. The note of the spring was just audible. Various secondaries (L_B) were wound for this representing from $L = 0.02$ to $L = 1.5$ henry. On testing a secondary which has its own primary (L_1, figure 4, where E is the battery—usually 3 cells with resistances—B the break apart from mechanism, P the primary both of L_B and L_1, C the condenser and T and T' the telephones kept in phase and to be connected by the acoustic pipe), the two primaries and secondaries were often with advantage joined in series, respectively, as the diagram indicates. The secondary L_B may be removed, using its primary only; or the primary of L_1 may be removed, as the magnitude of the inductance relations dictates.

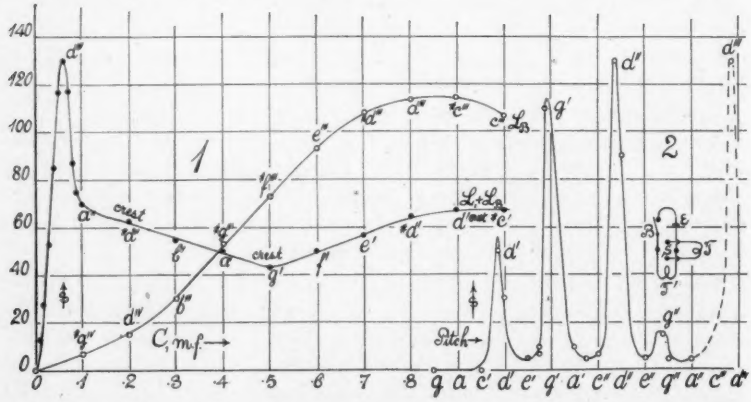
2. *Short Pipe.*—This was 10 cm. long between telephones and a scant centimeter in diameter. The pin hole probes (salient and reëntrant) were attached at the middle. The telephones vibrated in phase, so that odd harmonics should be ineffective; but these may stimulate other harmonics.

The survey in pitch is reproduced in figure 2. The insert is a diagram of the connections (S, a switch for T). Induction coils were purposely avoided, so that B is a motor periodic break. The interferometer fringe displacements, s, are given by the graph, indicating pipe harmonics about

a half semitone below d', g', d'', g'' and d''', the latter detected by the electric oscillation. The weak g'' is none the less definite. Probably the periodic break proves inadequate contact at these higher frequencies. No cusps were found below d'.

The graph L_B, figure 1, registers the electric oscillations when L_1 in figure 4 is removed, giving the fringe displacements or nodal intensity in the acoustic pipe when the capacity of the condenser, C, is increased in steps of 0.1 microfarad. The resonance crest (acoustic and electric) lies between $C = 0.8$ and 0.9 microfarad. If we take $C = 0.85$ microfarad since $\omega^2 = 10^7 \times 5.02$, for the note near d''', $L_B = 0.023$ henry.

With this datum the frequencies corresponding to $C = 0.1$, 0.2, etc., microfarad, may be computed and they are inserted to the nearest note on the graph, L_B. One notes the slow variation of pitch in the crest region as compared with the rapid changes near the anterior parts of the graph.

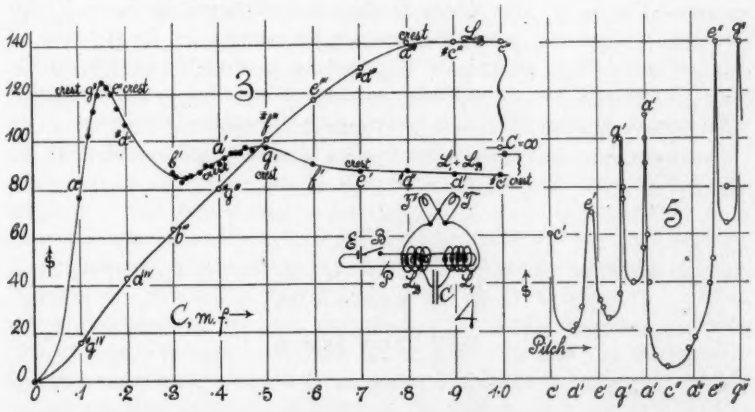


This accounts in part for the flatness of the crest. It may be sharpened by increasing the current (s); but there is then danger of sparking through the condenser unless it is specially constructed.

The additional inductance of coefficient $L_1 = 0.32$ was now added in series as shown by the diagram, figure 4, with a single interruptor for both primaries, and the secondaries also in series. The results obtained are summarized in figure 1, in the graph, $L_1 + L_B$. The crest is now near $C = 0.06$. If the note is the same slightly flattened d''', this crest gives a total inductance of $L = 0.33$ henry, a little short of the actual value, meaning that the crest estimate should be a little shifted.

With $L_1 + L_B = 0.34$, the ranges of pitch to the nearest note are as inserted in the graph at $= C$ 0.1, 0.2, etc. The approximate positions of the crests from figure 2 are also shown. With the exception of d''' and possibly d', they make no obvious impression in figure 1 and the acoustic

g' crest has actually dropped into an electric trough. As a whole the notes happen to lie about 2 octaves below the notes of graph L_B. The reasonable expectation that the troughs of the electric graphs should coincide with the troughs of the acoustic graphs is thus not admitted. The discrepancy is probably due to the differences in excitation. The direct current, periodically interrupted is under better conditions to force a vibration, than is the self-starting electric oscillation. This is an advantage, insofar as it limits a bewildering abundance of harmonics in the latter case. If C_0 is the step unit, so that $C = nC_0$ and if N_0 is the fundamental harmonic so that $N = n'N_0$, $n'^2n = 1/(8\pi^2N_0^2LC)$, a constant. Hence a series n'^2n, $n_1'^2n_1$, etc., is implied; but as a rule only one pair is conspicuous. Nevertheless the abnormal form of the graph L_1+L_B between a'' and g' suggests an elevating tendency, even if a continuous change of C does not, as a rule, improve the evidence.



3. *Long Pipe.*—The frequent occurrence of crests in the pitch survey with no equivalent in the electric oscillations (silent crests, as it were) suggested the trial of a long thin pipe (30 cm. in length, 1 cm. in diameter) which would naturally be able to harbor many nodes of high pitch. The acoustic behavior of this pipe is recorded in figure 5, which was difficult to construct satisfactorily by ear method, because of the sharpness and proximity of the cusps. The maxima e', g', a', e'', g'', stand out; but below c' there is intricacy hard to make out. Between e'' and g'' one is often at a loss and it was impractical to go higher.

Figure 3, curve L_B, summarizes the fringe displacements, s for changes of C of 0.1 microfarad each, when the small coil L_B above, is the secondary. In relation to location of maxima, the curve resembles the corresponding short tube curve, figure 1, L_B; but there is now no crest but rather an end plateau to the curve, after $C = 0.8$ microfarad is passed. If we take this

as the maximum, the note for L_B 0.023 will have to be d''' as in figure 1; such a note is out of immediate correspondence with figure 5; but otherwise not unexpected in its relation to g' and since the pipe is just 3 times as long as the short pipe. The distribution of notes in figure 1, L_B, may, therefore, again be taken here.

Adding L_1 to L_B as heretofore, the graph $L_1 + L_B$ of figure 3 is obtained, of which the notes for $C = 0.1$, 0.2, etc., microfarad must be the same as in the corresponding earlier curve of figure 1. This curve has actually captured two crests. If the lower one is taken at $C = 0.5$ and g' ($\omega^2 = 10^6 \times 5.91$), $L_1 + L_B = 0.34$ which is satisfactory. The upper crest is hard to identify relative to figure 5. As an e'' it is too low and as a g'' too high; but the latter is more probable. If the crest is put at $C = 0.14$ microfarad and the frequency g'', $L_1 + L_B = 0.30$ henry is the nearest approach. The crest found may be a superposition of the e'' and g'', recalling the vagaries of figure 5. The crests of the latter displayed on figure 3 indicate that g' and its harmonics dominate the curve $L_1 + L_B$ and that c', e', a', e'' are without relevance. The purpose of using the electric oscillations to interpret the astonishing presence of very low notes associated with very short thin pipes has, therefore, in a measure, succeeded.

* Advance note from a Report to the Carnegie Institute of Washington, D. C.

ON THE REFLECTION BY A CRYSTAL OF ITS OWN CHARACTERISTIC RADIATION

By William Duane

Jefferson Physical Laboratory, Harvard University

Communicated February 8, 1926

In a separate note[1] Dr. S. K. Allison has published his present opinion of the trustworthiness of certain data obtained in experiments on the X-radiation from a molybdenum target reflected by a crystal of KBr. I am very glad that Dr. Allison has published this note, for it helps to clear up certain questions relating to the reflection of X-radiation by such crystals as KBr, KI, etc.

The curve to which Dr. Allison refers represents very well the main features of the molybdenum spectrum reflected by KBr and observed by its ionizing effected in a chamber containing methyl iodide. On the curve can be seen: (*a*) the short wave-length limit of the continuous spectrum, (*b*) the abrupt decrease in the ionization current at the critical ionization wave-length of the iodine in the chamber, (*c*) the K-series lines of molybdenum, reflected in four orders (and even the γ-line in the fifth) and, (*d*)

the sharp rise at the critical absorption wave-length of the bromine in the crystal. Owing to the very great absorption of the KBr for X-rays of wave-lengths as long as those employed in these experiments, the curve drops off rapidly on the long wave-length side of the last-mentioned sharp rise (*d*), giving the appearance of a peak. This rapid decline in the intensity of the continuous spectrum with increasing wave-length is shown at several places on the curve in different orders of reflection, and is an important point in connection with the discussion that follows.

In addition to the features (*a*), (*b*), (*c*) and (*d*), mentioned above, the curve shows certain irregularities at points corresponding to the wave-lengths of the bromine K-series lines. These were interpreted as indicating the reflection by the crystal of its own characteristic spectrum. Unfortunately many of these lie so close to the strong molybdenum lines that it is impossible to draw conclusions from them. The spectrum at the Brγ and Brβ lines in the third order may have been incorrectly observed or recorded, as Dr. Allison suggests. In general, the γ and β lines lie so close to the critical absorption that it is not possible to distinguish between a line and a pure absorption peak, produced as described above. The α-doublet, however, is far enough away not to be interfered with by the absorption. Bearing these points in mind the writer himself examined the spectrum at the Brα line reflected in the second order, taking the readings of the electrometer many times. In every case the ionization current was larger at the Brα peak than on either side of it. At that time, three observers, one in addition to Dr. Allison and the writer, agreed that this was so. It may be that the particular curve to which Dr. Allison refers somewhat exaggerates the effect. The writer believes, however, that at least a few per cent more radiation was reflected at the bromine Kα line than in its immediate neighborhood. He has seen so often a similar excess of radiation reflected in the first, second and third orders at the Kα line of one of the chemical elements in the reflecting crystal that he is convinced that a crystal does sometimes reflect an appreciable amount of its own characteristic radiation. The crystal does not, however, reflect a perceptible quantity of its own characteristic radiation in experiments of the kind under discussion, if it has been carefully selected from the point of view of perfection by observing the accuracy with which an impression produced by reflected rays on a photographic plate corresponds with the size and shape of the spectrometer's slit system. This question has been discussed in a previous Note in these PROCEEDINGS.[2]

The best explanation of this excess radiation reflected by an imperfect crystal at an angle corresponding to a Kα doublet may be that suggested in the March (1925) number of these PROCEEDINGS of the National Academy on page 178. In applying the idea there expressed to the present case we must remember that, owing to the great absorption of the continuous

spectrum by the crystal, a very large part of the ionization current at a point in the neighborhood of the BrKα line reflected in the second order must be due to the fluorescent BrKα radiation emitted by the crystal more or less uniformly in all directions. The excess exactly at the line itself simply means that there is an increase in this fluorescent radiation emitted in that particular direction. In one of the first Notes published from our laboratory on this subject it was pointed out that a crystal must reflect that part of its own fluorescent radiation which, travelling in the proper directions, strikes reflecting planes at the reflecting angles as given by the Bragg law. At that time it was not thought this reflection could account for the observed phenomena. The solid angle, δ, within which the directions of monochromatic X-rays must lie in order that they be reflected from a given set of planes is extremely small and, therefore, the fraction of the total fluorescent radiation thus reflected by the planes of a perfect crystal must be small also. If, however, the crystal is not perfect, if, in particular, it has the kind of imperfections described in one of the last mentioned Notes in which the planes are displaced, but so as to remain approximately parallel to one of the crystal axes, then a much larger amount of the fluorescent radiation will be reflected. To fix our ideas suppose the spectrometer to be set for the reflection of X-rays having the wave-length of the Kα line, and consider the fluorescent radiation coming from a point, A, in the crystal. The ionization current due to the fluorescent radiation travelling straight from A to the ionization chamber depends upon the solid angle, S, subtended at A by the slit in front of the ionization chamber. The part of the fluorescent radiation from A which travels straight ahead in the direction of the primary beam will strike the reflecting planes at the proper angle for reflection and will be reflected into the ionization chamber. In the case of a perfect crystal, however, this reflected beam would produce a very small effect, for the solid angle, δ, within which the rays must lie in order to be reflected is much smaller than S. If, however, many of the planes in the crystal are displaced as above described, X-rays travelling in the general direction of the original beam and contained in a solid angle much greater than δ will find planes in the crystal at proper angles for reflection and will be thrown into the ionization chamber. If it happens that this solid angle is about equal to S a perceptible increase in the ionization current due to the reflected fluorescent radiation might occur. The relative magnitude of the effect would depend on the reflecting power of the crystal planes and upon differences in absorption due to differences in the paths traversed by the reflected rays and those travelling straight from A to the ionization chamber.

The breadth of a fluorescent line produced as described above depends upon the amount by which the reflecting planes departed from parallelism. In the case of a random distribution of planes such as in a finely divided

powder, one would not expect to observe a line, for the fluorescent radiation would be reflected more or less uniformly in all directions.

[1] Following paper in this issue, p. 143.

[2] Armstrong, Duane and Havighurst, *Proc. Nat. Acad. Sci.*, **11**, 218 (1925).

NOTE ON THE "SELECTIVE REFLECTION" OF X-RAYS BY CRYSTALS OF POTASSIUM BROMIDE

BY S. K. ALLISON

GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON

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Walter[1] has studied the reflection of X-rays by crystals of KBr by photographic methods, in an attempt to detect selective reflection of radiation having the wave-lengths of the K series of bromine. No such effect could be detected by a study of the photographs which he obtained. Later, in a paper by Allison and Duane,[2] a curve showing the results of an investigation by the ionization chamber method of the reflection of X-rays by KBr was published. This curve showed a very slight effect at the position of Br$K\alpha$ in the first order, and more positive indications of a selective reflection in higher order where the total intensity was quite low.

Armstrong, Duane and Havighurst,[3] continuing the investigation of the reflection of X-rays by alkali halide crystals, found that if the crystals were carefully selected for perfection, by observing the sharpness of the photographic registration of a reflected X-ray beam, no effects were obtained which could be ascribed to "selective reflection." Allison[4] had also found that no such effect existed in the reflection of X-rays by barite.

Recently Weber[5] and Kulenkampff[6] have carefully investigated the reflection of X-rays by KBr, using photographic methods. The spectra of Weber were obtained by the wedge-crystal method, while Kulenkampff tried both this method and the method of the rotating crystal in his attempt to detect the selective reflection. Both investigators conclude that no such effect can be detected in the spectra obtained from well-formed crystals, as was found by Armstrong, Duane and Havighurst.

Both Weber and Kulenkampff remark that it is difficult to understand how the Br lines in the higher order spectrum published by Allison and Duane can be explained as due to crystal imperfections. They are quite correct in this criticism. It is the purpose of this note to make plain that certain portions of the curve referred to[2] are now regarded by the writer as unreliable. In particular, no confidence can be placed in the portion

of the curve which indicates that in the third order there is a reflection of the BrKγ and Kβ lines of intensity comparable with that exhibited by the Mo Kα-doublet reflected in the usual manner in the fourth order. Later trials showed that although a slight excess of radiation probably existed at the position where reflection of the BrKα line in the second order would be expected, the curve under discussion gives an incorrect representation of its intensity relative to the adjacent molybdenum lines. This present opinion thus agrees with the experience of the investigators both in Jefferson Physical Laboratory and elsewhere, who have found no evidence of the reflection of characteristic radiation from KBr of any such magnitude.

[1] *Zs. Physik.*, **20**, 257 (1925).
[2] Allison and Duane, *Proc. Nat. Acad. Sci.*, **10**, 298 (1924).
[3] Armstrong, Duane and Havighurst, *Ibid.*, **11**, 218 (1925).
[4] Allison, *Amer. J. Sci.*, **8**, 261 (1924).
[5] *Zs. Physik.*, **33**, 767 (1925).
[6] *Physik. Zeit.*, **26**, 657 (1925).

SYSTEMATIC RELATIONS BETWEEN ELECTRONIC STRUCTURE AND BAND-SPECTRUM STRUCTURE IN DIATOMIC MOLECULES. I

By Robert S. Mulliken

Jefferson Physical Laboratory, Harvard University

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In the theory of electronic band spectra, as developed especially by Lenz, Heurlinger and Kratzer, the structure of bands is determined by changes in the state of rotation or precession of the molecule. These are limited, according to the correspondence principle, to changes of the resultant angular momentum j by ± 1 (P and R branches) or 0 (Q branches). The change $\Delta j = 0$ is permitted, however, only when the *motion* of the *emitting* electron in one or both states has a Fourier component parallel to the vector j. Reference may be made to a paper[1] of Kratzer for a more complete discussion.

Kratzer[1] and Kramers and Pauli[2] have obtained the following formula for the energy contribution due to molecular rotation or precession:

$$E^m = Bm^2 + \ldots\ldots = B(\sqrt{j^2 - \sigma^2} \mp \epsilon)^2 + \ldots\ldots\ldots \qquad (1)$$

Here σ is the component of the vector electronic angular momentum, which will here be called j_e, perpendicular to the nuclear angular momentum vector m, while ϵ is the component of j_e parallel to m; σ and ϵ need not have rational values, since they are not in general individually quantized.[2]

The double sign before ϵ was introduced by Kratzer, and corresponds to parallel and anti-parallel positions. In spite of objections of Kramers and Pauli based on considerations of dynamical stability, this double sign will be used here, since without it certain band spectra (e.g., the CH and the HgH type bands) seem incapable of explanation. On grounds of dynamical stability, σ is restricted by Kramers and Pauli to a position parallel to the figure-axis.

In the following the expression ϵ-type orbit or σ-type orbit will be used to denote briefly an electron orbit whose angular momentum vector is parallel or perpendicular to m.

. Three special cases of equation (1) may be distinguished. In the general case (1A), it is convenient to expand so as to get rid of the radical in (1). Cases (1B) and (1C) are obvious special cases. Adding the vibrational and electronic energies E^n and E^e to E^m, we have:

$$F(j) = E^e + E^n + B[(j \mp \epsilon)^2 - \sigma^2 \pm \epsilon\sigma^2/j + \ldots.] + \ldots\ldots \quad (1A)$$

$$F(j) = E^e + E^n + B(j^2 - \sigma^2) + \ldots\ldots\ldots \quad (1B)$$

$$F(j) = E^e + E^n + B(j \mp \epsilon)^2 + \ldots\ldots\ldots \quad (1C)$$

Assuming for the moment that the emitting electron moves in an essentially plane orbit, three cases which should give a Q branch may be distinguished: (1) σ present, due (at least in part) to the emitting electron; (2) σ present, but emitting electron in an ϵ-type orbit; (3) σ absent, but emitting electron in a σ-type orbit, its σ being neutralized by the action of other electrons. Case (3) should give the same (approximately Maxwell-Boltzmann) intensity distribution for the Q as for the P and R branches; in (1) the first few lines should be relatively weaker in the Q branch; in (2) only the first few lines should be of considerable intensity. Intermediate or mixed cases might also occur. Only case (1) seems to be known as yet in practise. The expected intensity of Q branches is in any case greatest if the causative factor is present in both initial and final states, and zero if it is present in neither state. The absence of a P or an R branch may sometimes be expected;[1] but such cases are as yet unknown in practise. In addition to the principles above discussed, there are certain additional restrictions on the occurrence of various branches; these will be discussed later.

The violet CN bands consist of a doublet P and a doublet R branch (thus altogether four branches). This structure is interpreted by Kratzer[3] as being due to a combination of two terms of type (1C), with $\epsilon = {}^1/_2$. He states "From the circumstance that no zero [Q]-branch is present, we must conclude on the basis of the correspondence principle that either it [ϵ] or the emission electrons can be replaced by an electron moving [in both initial and final states] in the plane of rotation [of the nuclei], whose radial quantum number [alone] changes." The material in brackets has been inserted by the writer. It will be seen in the following that by the well-

supported assumption of a single Na-like emission electron, important further results can be obtained. It should, however, be noted that Dieke[4] has suggested an alternative interpretation of the violet CN bands, according to which they consist of one P, one R and two Q branches; and Birge has suggested another interpretation.[5] The essential correctness of Kratzer's relatively simple interpretation will, however, be assumed here, and justified by the results obtained.

In a paper[6] on the spectrum of BO, the writer pointed out that the molecules BO and CN each have nine electrons outside their K shells. It was suggested that eight of these form a closed group, as in the Na atom, the ninth being loosely bound, perhaps in a 3_1 orbit, and giving rise when excited to the observed spectra. The idea of "octet" molecules of the above type was suggested by Langmuir's model[7] of the N_2, CO, CN^- and NO molecules. In a later paper,[8] it was suggested that the normal and second excited states of BO, CN, CO^+, N_2^+ and other analogous molecules containing one unused valence electron, may be of the nature of ^2S states (Russell-Saunders notation[9]), and the first excited state of the nature of a ^2P state. The supposed ^2S states are both characterized by a single electron level, and the ^2P state by a double level, as in Na. Furthermore, the molecular stability, as gauged by the vibration frequency and moment of inertia, is characteristically less when the electron is in the ^2P state than when it is in *either* of the ^2S states. Probably the strongest argument in favor of the octet structure for these molecules is the fact that the normal state of the most loosely bound electron is a ^2S (presumably a 3_1) state. If these molecules consisted merely of two atoms with unchanged quantum numbers for their electrons, the most loosely bound electron in each would be in a P (2_2) state.

The extension of these ideas of electronic multiplicity to molecules containing two (N_2, CO, etc.) or three (NO, etc.) electrons in excess of the number required to just form the group of eight, was also briefly suggested,[8] an analogy of these two groups of molecules to atoms of the Mg and Al types, respectively, being expected.

The applicability to band spectra of the alternation and displacement laws of line spectra, of which use has been made above, was first pointed out by Mecke,[10] and also independently by Birge (private communication). Mecke also pointed out,[11] independently of the writer, the existence of certain analogies between the spectra of CO^+ and N_2^+ and those of BO and CN. In the same paper, Mecke also considered the question of multiplicity in band spectra. But although some of his results superficially resemble those here obtained, his treatment seems open at two or three points to fatal objections; one of these has been discussed in a previous paper.[8] Mecke's work contains, however, several valuable suggestions to which reference will be made later.

Additional evidence on the occurrence of double electronic levels in band spectra has resulted from the work of the writer,[8,12] and of Mecke[13] on the spectra of the alkaline earth halides; and from Hulthén's work[14] on the ZnH, CdH and HgH bands. This will be discussed in a later paper.

The writer's suggestions in regard to electronic multiplicity in such molecules as N_2, CO and NO have been strikingly confirmed by recent work of Birge and Sponer. Birge has found[15,16] the expected odd multiplicity (singlets and triplets) in CO and N_2, and has also found stability relations similar to those above noted, for S and P states. From Sponer's work[17] one can conclude that the normal state of the NO molecule is a double ^2P state, just as in the case of the Al atom, while the first excited state is a ^2S state. Further, the molecular stability is less in this P state than in the S state, in agreement with the rule found to hold in molecules of the CN type. These results seem to constitute very strong support for the existence of the octet structure in all the molecules mentioned.

On the basis of the above and similar results, Birge recently made an important step in definitely postulating[16] that "the energy levels associated with the valence electrons of molecules agree in all essential aspects with those associated with the valence electrons of atoms." In the same paper, to which reference should be made, Birge attributes the greater stability of the molecule for S orbits as compared with P orbits, to the greater penetration of the electron in the former case, with resultant increase in the binding.

The above-stated postulate of Birge now stimulated the writer to the development of earlier tentative ideas. Kratzer's analysis of the violet CN bands involves the important assumption that j is integral; he then concludes, since m is half-integral, that $\epsilon = 1/2$. With the added postulate of a single emitting electron which undergoes transitions between two ^2S states, Kratzer's use of the correspondence principle (see above) will now at once lead to two definite conclusions: (1) In these S states, the lower of which is probably[6] the normal state of the CN molecule, the ninth outer electron moves in an orbit—presumably an elongated orbit passing around both nuclei—in the plane of nuclear rotation. (2) We can now identify ϵ with j_e, and conclude that the electron, either alone or as a result of its interaction with the molecular core, is associated with a resultant angular momentum of $1/2$ quantum—precisely as Sommerfeld assumes for the ^2S states of the Na atom.

Before attempting to extend the above method to other spectra, it will be well to justify if possible the assumption of an electron orbit of the type described. Such justification meets with two difficulties which arise from the fact that the force field is not central. In the first place, the existence of a periodic orbit here cannot be accounted for by ordinary mechanics.

But this difficulty seems to be little more than an exaggerated form of that which occurs in accounting for periodic electron orbits in all *atoms* containing more than one electron.

The second difficulty consists in the fact that the electronic angular momentum cannot be constant. But in the atomic case it is the constant *sum* of the electronic and nuclear angular momenta which is quantized. The molecular case differs only in that the nuclear angular momentum is no longer small and that the electronic and nuclear angular momenta are no longer *individually* constant. This appears, however, to do no violence to the spirit of the quantum theory; in fact, a similar generalization seems to be required in the case of *atoms* which possess more than one electron. The molecular case is characterized by a rapid interchange of comparatively large amounts—perhaps a few quanta—of angular momentum between nuclei and electron, the total angular momentum, however, being small and constant. This implies a small-amplitude librational motion of the nuclei, superposed of course on the ordinary rotation. The small amount of energy possessed by the nuclei in this form should give a real, but probably in all cases undetectably small, electronic isotope effect.

By a consideration of the structure of known band spectra, taking into account the occurrence of apparent nearly integral and half-integral rotational quantum numbers, the "missing lines" near the band-origins, the occurrence of P, Q and R branches, and the nature of the electronic multiplicity, the following simple postulates were constructed. Conversely, by the application of these postulates, the above features can be accounted for (in many cases for the first time) in all band spectra which the writer has examined carefully; and in no case has a definite contradiction been found. Predictions have been made as to bands whose structure has not yet been analyzed, and so far as can be seen from a preliminary examination, these are verified. It is of course likely that the following postulates and conclusions will need modification, but it is believed that they are at least a step in the right direction.

Postulates.—1. The electronic state of every molecule can be characterized, in accordance with Birge's recent postulate, by a term-designation (e.g., ^1S or ^2P); this is associated with an electronic quantum number j_e identical (at least substantially) with *Sommerfeld's* atomic inner quantum number j for the given term-type. Or in some cases (e.g., CH) each atom may have its own individual j_e, uncombined with that of the other atom.

2. The vector or vectors j_e set themselves parallel (ϵ components) or perpendicular (σ components), or nearly so, to the vector m, and the rotational energy term is given by a Kratzer-Kramers and Pauli formula (Eq. 1 above).

3. The molecular j has integral values for odd molecules, half-integral

values for even molecules, and is subject to the selection principle $\Delta j = 0, \pm 1$, the occurrence of P, Q and R branches being determined in accordance with the correspondence principle, as already discussed.

A detailed account of the application of these postulates to individual band spectra, and discussion of the problems of molecular structure, and of "rotational doubling" in band spectra, will be given in separate papers. The following remarks, which are partly in the nature of conclusions, will help to elucidate the postulates above. Following these remarks, a summary of some of the main conclusions resulting from the application of the postulates is given; the last two of these should be of some importance for the theory of line spectra and atomic structure.

Supplementary Remarks.—1. The usual selection principles for the azimuthal and inner quantum numbers of the electron are suspended, at least in that free combination of two ^1S or of two ^2S terms is permitted.

2. In the usual case where there is only one j_e, it can readily be seen that this has integral values when j has half-integral values, and *vice versa*.

3. When the rotational term is of the form of equation $(1C)$, there are usually two sets of rotational terms corresponding to two slightly different sets of m values, due to $\pm\epsilon$ combined with the fact[18] that ϵ usually deviates somewhat from an exact integer or half-integer. This *may* sometimes be due to an inexact parallelism of m and j_e; if so, there must be a small σ component (Eq. $1A$ then being applicable), but too small to affect appreciably the term values. There is also evidence (inequality of $+\epsilon$ and $-\epsilon$, etc.)[18] of a deviation of j_e itself from exact integers or half-integers (in known cases these have only the values 0 and $^1/_2$; this is explained by conclusion 1 below). The deviations of ϵ from integers or half-integers are usually least for stable molecules.

4. When the rotational term is of the form of equation $(1B)$, there is again usually a rotational doubling characterized by a small $\pm\epsilon$ (or by two values of ϵ, or a double value of B—or even also of E^ϵ, for very unstable molecules), so that equation $(1A)$ is again applicable. Possible explanations are in part analogous to those under remark 3.

5. As pointed out especially by Mecke,[10,19] P and R branches are usually characterized by a *conservation* of sign of ϵ between initial and final states, but Q branches by a reversal of sign; this is, however, not quite the whole story in the case of the Q branches.

6. In ^1S terms, rotational doubling is characteristically lacking; such terms act, in their combinations with ^1P terms, like *one* only of the usual pair of rotational levels.

Conclusions.—1. In most molecules whose spectra have been investigated, the orbits of the outer electrons are of the ϵ type for S states, and of the σ type for P or D states. This may perhaps be correlated with the relatively more elongated nature of the S orbits. In H compounds, the

H electron probably moves in an ϵ-type orbit ($\epsilon = {}^1/_2$) which in the case of odd atoms (in CuH, AgH, AuH, AlH) and in excited (^2P) states of certain even atoms (in ZnH, CdH, HgH), is coupled with a ^2S atomic electron, diminishing the multiplicity of the free atom by one. In the case of even atoms, the H electron orbit is generally not coupled with that of an electron of the other atom; such atoms in the ^1S state form loose compounds in which the resultant molecular state may be described as ^2S, or may equally well be regarded as two separate atoms in ^1S and ^2S states, respectively; this loose type of union is sometimes preserved in the (σ-type) ^1P states of the heavier atom (CH and OH bands), or sometimes replaced by a coupled type of union (ZnH, CdH, HgH—see above).

2. The presence of two nuclei with their two sets of K electrons produces no effect on the multiplicity; the latter appears to be determined solely by the valence electrons. This is contrary to the idea that the core has a resultant angular momentum which resides in the K electrons, and in line with the recent theory of Pauli.[20] This conclusion can be avoided, to be sure, by the rather forced hypothesis that the two separate K shells may so orient themselves as to give the same resultant effect as a single K shell in an atom.

3. Sommerfeld's j values (cf. postulate 1) each represent a *true* resultant electronic angular momentum of the molecule, or in view of conclusion 2, probably of the valence electron itself. Furthermore, the H atom has the value $j_e = {}^1/_2$, like an alkali metal atom; this is in accord with recent suggestions of Goudsmit and Uhlenbeck, and of Slater.[21]

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SYSTEMATIC RELATIONS BETWEEN ELECTRONIC STRUCTURE AND BAND-SPECTRUM STRUCTURE IN DIATOMIC MOLECULES. II. THE ZnH, CdH AND HgH MOLECULES AND THEIR SPECTRA

BY ROBERT S. MULLIKEN

JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY

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Introduction.—In a previous paper,[1] which will here be referred to as *I*, certain postulates were set up for the interpretation and prediction of the structure of band spectra. These will be applied in the present paper to the very instructive spectra of ZnH, CdH and HgH and in subsequent papers to the spectra of other molecules.

In the analysis of band spectra, the application of the Ritz combination principle does not yield directly the rotational energy function $F(j)$—cf. *I*—for the molecule, but only *differences* of this function, of the forms $\Delta_2F(j) = F(j+1)-F(j-1)$, from P,R combinations, and $\Delta_1F(j) = F(j+1)-F(j)$, from P,Q,R combinations. The general expressions for these, corresponding to the expanded form (Eq. 1*A*) of equation 1 of *I* are:

$$(2A)\quad \Delta_1F(j) = 2B(j + \tfrac{1}{2} \mp \epsilon) \mp B\epsilon\sigma^2/j(j+1) + \ldots\ldots$$
$$(3A)\quad \Delta_2F(j) = 4B(j \mp \epsilon) \mp 2B\epsilon\sigma^2/(j^2-1) + \ldots\ldots$$

From equations (2*A*) and (3*A*) it will be seen that the simultaneous presence of ϵ and σ can be determined experimentally from ΔF only when both ϵ and σ^2 are reasonably large. If *either* ϵ or σ is *alone* present (or if either is so small that $\epsilon\sigma^2$ is too small to detect), equations (2*A*) and (3*A*) assume the empirical forms $\Delta_1F = 2B(T + \frac{1}{2} \pm \gamma)$ and $\Delta_2F = 4B(T \pm \gamma)$. Here $\gamma << \frac{1}{2}$, and T, which will be called the effective rotational quantum number, has in practice nearly integral values (τ), or half-integral values (τ^*). From ΔF alone it is thus impossible to distinguish between the cases (1) σ appreciable, ϵ absent (or very small); (2) σ absent (or very

small), ϵ appreciable; (3) both ϵ and σ small or absent; the indistinguishability of cases (1) and (2) was first pointed out to the writer by Prof. E. C. Kemble. E.g., half-integral T values may arise *either* from half-integral j values, with $\epsilon = 0$, and σ present or absent, *or*, from integral j values with $\epsilon = \pm \frac{1}{2}$, and σ absent; integral T values (such as occur in the initial states of the HgH type bands) are comparatively rare in known bands, but their occasional occurrence is very significant. Escape from these ambiguities is afforded by the postulates, especially 3, of I, and the correctness of the results is attested by their complete consistency in all cases so far investigated.

It will frequently be necessary in the following to distinguish between terms for which ϵ is positive (parallel to m) and those in which it is negative (anti-parallel position). The former will be given the subscript 1, the latter, the subscript 2; thus $F_1(j) = B(j-\epsilon)^2 + \ldots$, while $F_2(j) = B(j+\epsilon)^2 + \ldots$. This nomenclature will also be extended to certain cases where there is a double rotational term of the σ type, with $\epsilon = 0$, or nearly so, or having two numerically different values of ϵ; in such cases the choice of designation is determined by analogy in behavior to the more usual cases.

Distinction between a more and a less excited state will be made by attaching superscripts—thus F', B', ϵ', etc., will refer to the *more excited* electronic state, F'', B'', ϵ'' to the *less* excited state.

In general, six branches are then to be expected for any band, as follows (cf. I, supplementary remark 5): $P_1(j) = F_1'(j-1) - F_1''(j)$; $P_2(j) = F_2'(j-1) - F_2''(j)$; $Q_1(j) = F_2'(j) - F_1''(j)$; $Q_2(j) = F_1'(j) - F_2''(j)$; $R_1(j) = F_1'(j+1) - F_1''(j)$; $R_2(j) = F_2'(j+1) - F_2''(j)$. It will be seen that P, Q and R branches are here implicitly defined as branches for which Δj has the respective values $+1$, 0 and -1. The *appearance* of any branch is determined by the values of B and Δm, and from this standpoint, a considerable variety of band-types is to be expected—and is observed. Also there are types in which various branches are missing, or in which certain branches are coalescent.

As stated in I, the Russell-Saunders notation will be used in designating electronic states.

Interpretation of ZnH, CdH, HgH Bands.—The spectra of these molecules have been studied in recent years especially by Hulthén[2,3] and by

TABLE 1

DOUBLET AND TRIPLET SEPARATIONS FOR 2 P TERMS

	MeH	M($^2P_{1,2}$)	Me($^2P_{1,2}$)	Me($^2P_{0,1}$)	Me$^+$($^2P_{1,2}$)
Zn	330	248 (Cu)	389	190	874 (?)
Cd	1001	921 (Ag)	1171	542	2482
Hg	3683	3815 (Au)	4630	1767	9829 (??)

Kratzer.[4,5] The evidence that the emitters are those named seems conclusive.[4,6,7] For each molecule, there are two closely related band systems having a common final state. Hulthén has shown an important

parallelism between these two systems and the transitions $2\ ^3P_{1,2}-1\ ^1S$ of the respective metal atoms.[8] The writer, however, believes that the correct formulation is $^2P_{1,2}-^2S$. The observed separations P_1-P_2 are compared in table 1 with the doublet separations of the comparable atoms Cu, Ag, Au, with the triplet separations of Zn, Cd and Hg, and with the doublet separations of Zn^+, Cd^+ and Hg^+.

The recorded observations on intensity[2,9] indicate that the low-frequency systems of ZnH, CdH, HgH are more intense than the high-frequency systems, and so suggest that the ^2P doublet is inverted. But this is conclusively disproved by the evidence from the missing lines (see below). One might, then, conclude that the intensity rules of line spectra are inapplicable here, but such a conclusion is hardly justified as yet.[9]

Table 2 shows that the molecular stability, as gauged by the vibration frequency ω_0 and the nuclear separation r_0, is markedly greater for the more excited states of the molecule; this relation was first pointed out by Hulthén,[3,8] also by Ludloff.[5] The correlation of r_0 with the ionization potential of the metal is no doubt due to the fact that the latter should vary qualitatively inversely as the atomic or ionic radius; thus the equilibrium distance between the nuclei of the two atoms is evidently largely dependent on the radius of the metal atom or ion. A completely parallel variation of r_0 with the ionization potential of the atom occurs in the series CuH, AgH, AuH. The comparatively large values of r_0 show, as pointed out by Kratzer,[4] that the union of the H and metal atoms is here quite different in character from that in HCl, HBr and the like, where the H^+ ion loses its electron and penetrates the outer shell of the negative ion.

TABLE 2

MOLECULAR CONSTANTS FOR ZnH, CdH AND HgH*

		B'	r_0'(A.U.)	ω_0'	T'	B''	r_0''	ω_0''	T''	ION. POT. OF Me
ZnH	P_1	7.15	1.54		$\tau\pm0.01$	6.54	1.60	1552	$\tau^*\pm0.01$	9.35 v.
	P_2	7.47	1.50		$\tau\pm0.00$					
CdH	P_1	5.96	1.67		$\tau\pm0.02$	5.33	1.76	1374	$\tau^*\pm0.03$	8.95 v.
	P_2	6.03	1.66		$\tau\pm0.00$					
HgH	P_1	6.56	1.60	(1995)	$\tau\pm0.13$	5.38	1.74	1308	$\tau^*\pm0.095$	10.39 v.
	P_2	6.61	1.58	(2180)	$\tau\pm0.00$					

* The data are taken from, or based on, the papers of Hulthén, Kratzer and Ludloff. The ω_0'' values, and the ϵ values for HgH, are revised values kindly supplied by Prof. R. T. Birge. The ω_0' values are calculated from a theoretical relation between ω_0, B and the coefficient of j^4.

In both band systems, for each emitter, each band has six branches, for which $\Delta T = -1\frac{1}{2}, -\frac{1}{2}, +1/2, -1/2, +\frac{1}{2}, +1\frac{1}{2}$, and which are due to combinations of the two τ-type initial and two τ^*-type final terms; these branches are interpreted by Kratzer[4] as R_1, R_2, Q_1, Q_2, P_1, P_2, respectively. For the representation of these bands Kratzer has assumed equations of the form (cf. I) of equation ($1C$) for both states, but with an

added linear term $\pm 2\delta j$. His values of δ are small, and he concludes $\epsilon' = 0$, $\epsilon'' = \frac{1}{2}$, for ZnH and CdH[4,10] and for the high-frequency system of HgH[5]; but for the low-frequency system of HgH, his δ values are large, and he concludes $\epsilon' = \frac{1}{2}$, $\epsilon'' = \frac{1}{4}$. It seems to the writer that the close analogy shown in table 2 between the spectra of the three molecules is nearly conclusive evidence against this special interpretation of Kratzer's for one system of HgH bands, in spite of Kratzer's very strong evidence in its favor; this evidence consists (ref. 4, p. 93) in certain numerical relations which must now apparently be regarded as fortuitous, although the matter deserves further investigation. Furthermore, the theoretical justification of Kratzer's linear term has been called in question by Birge and Kemble.[11] The observed ΔF values can be expressed without the use of a linear term, by using ϵ values which depart somewhat from exact integers or half-integers (and which may increase[12] with j). Table 2 then shows a very systematic variation with atomic weight in the departures of ϵ from 0 or $\frac{1}{2}$.

A formally comparatively slight change in Kratzer's interpretation (as already modified above by the suppression of the linear term) of the HgH type bands serves to make them fit the postulates of *I*. Integral values of j, required for odd molecules by postulate 3, have already been assumed by Kratzer. From table 2, ϵ'' has in all cases approximately the value $\frac{1}{2}$. Also, $\sigma'' = 0$, or nearly so, for otherwise an $\epsilon\sigma^2$ term in $\Delta F''$ would have made itself evident. For both initial states, $\epsilon' = 0$, approximately, but, as shown in the introduction, we cannot determine from the $\Delta F'$ values whether or not a σ is present. But the presence of Q branches—their intensity is about the same as that of the P or R branches—gives evidence (although not in itself conclusive—cf. *I*, paragraph 5), in favor of the presence of a σ due to the emitting electron. In view of the evidence that the two initial electronic terms are $^2P_1$, and $^2P_2$, the assumptions $j'_e = \frac{1}{2} = \sigma'$ (approximately) for the low-frequency systems, and $j'_e = \frac{3}{2} = \sigma'$ (very nearly) for the high-frequency systems, seem justified. The assignment of $j'_e = \frac{1}{2}$ to the apparently more intense system is based upon the evidence of the "missing lines."

The deviations of ϵ' from 0 and of ϵ'' from $\frac{1}{2}$ are largest in the HgH bands. If $j'_e = \frac{1}{2}$ or $\frac{3}{2}$ exactly, the deviations must mean that σ' falls below $\frac{1}{2}$ or $\frac{3}{2}$, and similarly, if $j''_e = \frac{1}{2}$ exactly, that $\sigma'' \neq 0$. Then from j_e and ϵ we can in each case calculate σ, since $j^2_e = \epsilon^2 + \sigma^2$. The following equations result (for higher power terms, cf. refs. 4, 5); in each case the upper sign of ϵ belongs to F_1, the lower to F_2:

$$(4)\quad \begin{cases} F'_{1,2}(P_2) = 6.61(\sqrt{j^2-(1.500)^2} \mp 0.00)^2 + \cdots\cdots \\ F'_{1,2}(P_1) = 6.56(\sqrt{j^2-(0.483)^2} \mp 0.13)^2 + \cdots\cdots \\ F''_{1,2}(S) = 5.38(\sqrt{j^2-(0.294)^2} \mp 0.405)^2 + \cdots\cdots \end{cases}$$

Here σ'' is surprisingly large; nevertheless it will be seen by a consideration of numerical magnitudes in equation $(2A)$ that the effect of the $\epsilon\sigma^2$ term in $\Delta F'(P_1)$ and in $\Delta F''$ will be detectable only by very accurate measurements on the lines of lowest j; the data now available seem inadequate for a decision. In the cases of CdH and ZnH, the calculated σ'' values are very small.

The "missing lines" of a band are determined—in a way originally pointed out by Lenz—by the fact[13] that, in equation (1) of I, j cannot be less than σ. This rule determines, for each of the six terms of equation 4, a minimum value of j, which may be denoted $j_{\text{min.}}$. These values are 2 for $F'_{1,2}(P_2)$, 1 for $F'_{1,2}(P_1)$ and 1 for $F''_{1,2}$. In any particular branch of a band, the smallest possible *pair* of j values (j', j'') is determined, in a fairly obvious manner, sometimes by $j'_{\text{min.}}$, sometimes by $j''_{\text{min.}}$.

For the transition $(P_1 \longrightarrow S)$ here, the predicted first lines for the various branches are, in terms of initial and final j values $(j' \longrightarrow j'')$: $P_{1,2}$, $(1 \longrightarrow 2)$; $Q_{1,2}$, $(1 \longrightarrow 1)$; $R_{1,2}$, $(2 \longrightarrow 1)$. The *observed* first lines as recorded by Hulthén[2,3] are (a * means that the observed line is superposed on another line, so that the result is not wholly conclusive): ZnH λ 4326, $P_1(1 \longrightarrow 2)$; $P_2(1 \longrightarrow 2)$; $Q_1(1 \longrightarrow 1)$*; $Q_2(1 \longrightarrow 1)$; $R_1(2 \longrightarrow 1)$*; $R_2(2 \longrightarrow 1)$, but the calculated position of $R_2(1 \longrightarrow 0)$ is practically the same as for $Q_2(1 \longrightarrow 1)$, so that the result is inconclusive for R_2; CdH λ 4510, $P_1(1 \longrightarrow 2)$; $P_2(3 \longrightarrow 4)$; $Q_1(1 \longrightarrow 1)$; $Q_2(3 \longrightarrow 3)$; $R_1(3 \longrightarrow 2)$; $R_2(3 \longrightarrow 2)$, but here and in HgH λ 3728 the data are doubtless incomplete; in HgH λλ 4017 and 4219, where the data are most reliable, the agreement with prediction is complete. The agreements above noted are extremely satisfactory, in view of the experimental uncertainties. However, the absence of lines for which j' or $j'' < 1$ cannot be considered quite *conclusively* proved without further very careful study; nevertheless, there appears to be no definite evidence in Hulthén's data for the presence of any such lines.

In its prediction of missing lines for the bands above considered, the present interpretation differs from Kratzer's only in one respect. The absence of lines for which j' or j'' is zero is here attributed to the presence of an appreciable σ, whereas Kratzer was forced to make the arbitrary assumption that $j = 0$ is excluded. In a later discussion of the CH bands, however, it will be shown that this arbitrary exclusion is definitely not justified, since at least one line is unquestionably present for which $j' = 0$, σ also being zero. Hence the observed absence of $j' = 0$ and $j'' = 0$ in the present case is strong evidence in favor of the assumed existence of a σ' and a σ''.

For the transition $(P_2 \longrightarrow S)$, the predicted first lines are: $P_{1,2}(2 \longrightarrow 3)$; $Q_{1,2}(2 \longrightarrow 2)$; $R_{1,2}(2 \longrightarrow 1)$. These are precisely the *observed* first lines in ZnH λ 4260 [Hulthén gives also $P_1(1 \longrightarrow 2)$ and

$P_2(1 \longrightarrow 2)$, but both are*], in CdH λ 4300 [except that Hulthén reports $P_1(1 \longrightarrow 2)$, but the recorded line is exceedingly weak and slightly displaced] and in HgH λ 3500.[2,3] Since the missing lines in these bands have not hitherto been explained and could not be explained by Kratzer's interpretation, the correctness of the present interpretation for both systems of bands seems very strongly supported by this evidence.

The low stability of the HgH molecule in the ^2S state is shown especially by Hulthén's work,[3] in which he finds from the spectrum a heat of dissociation corresponding to only 0.37 volt. Although the impossibility of determining directly the existence of a small σ'' makes impossible a *direct* exact evaluation of j_e'' ($j_e'' = \sqrt{\epsilon''^2 + \sigma''^2}$), our assumption $j_e'' = \frac{1}{2}$ (or nearly so) is obviously strongly supported by the observed ϵ'' values, and by the testimony of the missing lines, for HgH, CdH and ZnH. The molecule in its less excited state may then in each case be pictured as composed of a neutral, relatively inert, metal atom in its normal ^1S state ($j_e = 0$), to which the H atom ($j_e = \frac{1}{2}$) is loosely attached by secondary (van der Waals) forces, converting the ^1S state of the atom into a ^2S molecular state (cf. conclusions 1 and 3 in *I*). The orbit of the H electron is then approximately of the ϵ-type, $\epsilon = \pm \frac{1}{2}$ corresponding to a rotation of the electron in the same or opposite sense, respectively, to that of the nuclei.

The greatly increased stability of the molecules in their P states can be explained as follows: *one* of the metal valence electrons becomes excited and passes into an essentially σ-type 2_2 orbit, while the remaining n_1 electron becomes coupled with the 1_1 H electron so that $j_e = 0$ (or nearly so) for this pair of electrons. The nature of this coupling is doubtless the same as that which occurs in CuH, AgH, AuH and probably AlH, and will be discussed later in connection with the spectra of these molecules. The 2_2 electron is now in the same condition as in a doublet atom, hence there are two terms $^2P_1$ and $^2P_2$. The fact that the doublet separations in ZnH, CdH and HgH, respectively, agree well with those of neutral Cu, Ag or Au atoms (table 2), shows that the two electrons in n_1 orbits exert a considerable screening effect.

The considerable difference in r_0 (table 2) for the P_1 and P_2 states indicates a real difference in shape or position of the electron orbits in the two cases; and the marked difference in the ϵ values is also undoubtedly significant.

For the P_2 states, the existence of a double (perhaps even quadruple) rotational term F_1', F_2', in spite of the absence of an appreciable separation of a $\pm\epsilon$ or any other type between the term values, is shown unquestionably by certain perturbations.[3,5] The vanishing of ϵ probably shows that the electron orbit—which would here be expected to be truly circular—lies in a plane exactly perpendicular to the figure-axis.

The non-vanishing of ϵ in the case of the P_1 orbit indicates that the latter is *inclined* with respect to the internuclear axis. It seems possible that this is due to a tendency of the solitary P electron to become coupled with the other metal electron. Similarly, the presence of a σ in the final state might be due to a tendency of the isolated H electron to become coupled with one of the metal electrons, thus forcing the other into a different plane.

The assumption that j_e can divide itself between ϵ and σ has been shown, in the case of the transition $P_1 \longrightarrow S$, to afford a simple explanation (1) of the occurrence of deviations of ϵ from 0 or $\frac{1}{2}$ in connection with the phenomenon of rotational doubling, and (2) of the otherwise inexplicable absence of the state $j'' = 0$. But the persistence of rotational doubling for orbits of the σ- type, even when ϵ vanishes (P_2 states here; spectrum of AlH, etc.), shows pretty definitely that this doubling must arise from a deeper cause, of which the above deviations are but one manifestation. The writer hopes to discuss the problem more fully in a later paper. Whatever may be the ultimate explanation of rotational doubling, it is, however, evidently very important to make conclusive the already very strong evidence that j_e can be divided between ϵ and σ (the simultaneous presence of ϵ and σ in the final state of the CH bands is probably due to the *separate* j_e values of the two atoms). New very accurate measurements on the lines of small j in the HgH bands, and conclusive proof of the absence, in the bands of the low-frequency system, of the lines R_2 $(1 \longrightarrow 0)$ and $R_1(1 \longrightarrow 0)$, should settle this question. But, as will be shown in later papers, it is probable that in *most* band spectra the apparent deviations of ϵ from 0 and $\frac{1}{2}$ cannot be accounted for as here by the presence of a σ, but are probably due to some as yet unknown cause, so that something like Kratzer's linear term may after all be applicable.

Since, according to the postulates of I, the structure of a band system depends only on the type of electronic transitions involved, we may expect for the transition $^2P_{1,2} \longrightarrow {}^2S$ in *all* molecules a structure essentially the same as in the HgH bands; and for $^2S \longrightarrow {}^2P_{1,2}$ a structure differing only in respect to the missing lines—assuming, however, in both cases that the S orbit is of the ϵ type and that the P orbits are of the σ type. As will be shown in a later paper, these expectations are confirmed, so far as can be seen from the available data, in the cases of the BO, CN, CO^+, NO and alkaline earth halide bands.

[1] R. S. Mulliken, these PROCEEDINGS, March, 1926.

[2] E. Hulthén, Dissertation, Lund, 1923, "Über die Kombinationsbeziehungen unter den Bandenspektra."

[3] E. Hulthén, *Zeit. Physik*, **32**, 32 (1925)—HgH bands.

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[7] K. T. Compton and L. A. Turner, *Phil. Mag.*, **48**, 360 (1924); *Physic. Rev.*, **25**, 606 (1925); Compton, McCurdy and Turner, *Physic. Rev.*, **24**, 608 (1924); etc.

[8] E. Hulthén, *Nature*, Oct. 31, 1925.

[9] Dr. Hulthén has been so kind as to inform the writer that the high-frequency system is *much* weaker than the low-frequency system in HgH, *decidedly* weaker in CdH and about *equally intense* in ZnH. It seems likely that the conditions of excitation play a dominant rôle, masking the effect of the difference in à priori probabilities of the two excited states. Howson's CdH photographs (*Astrophys. J.*, **36**, 291, 1912) agree with Hulthén's statement.

[10] This includes an alteration of his published values[4] of δ' and ϵ' for ZnH (private communication).

[11] Cf. E. C. Kemble, *J. Opt. Soc. Amer.*, **12**, 1 (1926): footnote on p. 4.

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THE ELECTRONIC STATES OF THE HELIUM MOLECULE

By Robert S. Mulliken

Jefferson Physical Laboratory, Harvard University

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Extending tentative suggestions of the writer,[1] Birge has recently[2] made an important step in putting forward the hypothesis, which he supports by much valuable evidence, that the electronic states in molecules are essentially similar to those in atoms—so that, in particular, the molecular states may appropriately be designated by term symbols (^1S, ^2P, etc.), corresponding to those used (notation of Russell and Saunders) in line spectra. In applying this hypothesis to the structure of various band spectra, the writer has found that it leads successfully to many interesting results which will be discussed in separate papers. In the course of this work, a study of the structure of the helium bands gave definite evidence in favor of the designation $2S$–mP (m = 3, 4, 5. . .), the terms being of a singlet type, for the "main" series of helium bands, which have been found to obey a line series law[3,4]; and in favor of an identical designation in the case of the "second" series of bands. This evidence will be given in a later complementary paper.

It seems possible that the relatively intense "main" series is emitted by a molecule composed in its least excited state of two helium atoms in metastable $2S$ "doublet" states, and the weaker "second" series by a molecule composed of two metastable $2S$ singlet atoms; the evidence is given in the last paragraph. The relative intensity of the two systems is then qualitatively what might have been expected on the basis of stability

considerations. The fact that the molecular electron levels closely resemble those of the helium atom indicates, however, that the union is a very loose one even in the first case. Further strong evidence of instability appears in the absence of more than one band corresponding to each electron transition. This fact, as Curtis has pointed out, probably means that the molecule is too unstable to be capable of possessing even one quantum of vibrational energy in any of its electronic states. The instability is further shown[4,5] by the sudden rapid fading out of the bands, accompanied by evidence of a rapid increase in the moment of inertia, when the rotational quantum number passes certain not very large values.

In addition to the "main" and "second" series of helium bands, three other bands, at λλ 6400, 4546 and 5730, have been analyzed by Curtis.[5] Kratzer has shown[6] that these three bands have the same final electronic state. Curtis has suggested that the bands λλ 6400 and 4546 form the first two members of a line series. The band λ 5730 is, however, of markedly different structure from *all* the remaining bands, in that it has six branches while all the others have only three, and also in that its initial state is more stable (as shown by the relative moments of inertia) than its final state. The writer's study of the structure of these bands gives strong evidence that λ 6400 and λ 4546 correspond to a transition of the type xP–mS, and λ 5730 to xP–mD. This evidence indicates in particular that the electronic inner quantum number j has (in Sommerfeld's notation) the value 1 for all the P terms (here as well as in the "main" and "second" series bands), and the value 2 for the D term. That the S terms are such is indicated by the existence of certain restrictions in their combinations with P levels (appearance of only three branches instead of the six which appear for $D \longrightarrow P$) and by the analogy in band-structure of the $P \longrightarrow S$ and $S \longrightarrow P$ transitions here to that observed in similar bands of other molecules (CO, AlH) where it can be shown more directly that $j = 0$ for the S state.

In the analysis of the helium bands, the writer has adopted Mecke's valuable suggestion[7] that alternate lines are completely missing. This gets rid of the quarter-integral quantum numbers used by Kratzer and by Curtis, giving half-integers instead. It also doubles the calculated values of the internuclear distance r_0. It halves the calculated vibration frequencies ω_0, which in the helium bands cannot be obtained directly, but only by means of a theoretical relation between two of the rotational energy coefficients. The new values are as follows: from Kratzer's analysis, for the final state of λλ 4546, 6400 and 5730, $r_0 = 1.07\,A$, $\omega_0 = 1760$ wave-number units; λ 6400 initial state, $r_0 = 1.08\,A$; λ 4546 initial state, $r_0 = 1.09\,A$; λ 5730 initial state, $r_0 = 1.05\,A$, $\omega_0 = 1535$; from Curtis and Long's work, $2S$, $r_0 = 1.05\,A$, $\omega_0 = 1780$; $3P$, $r_0 = 1.08\,A$; thence increasing to $1.12\,A$ for the (P,R) state $8P$, while for ω_0 the mean value for the states

$3P$ to $6P$ is 1695. In all cases there is a large probable error in the ω_0 values; in particular, the large negative deviation of ω_0 for the λ 5730 initial state is probably incorrect, since Mecke[8] and Birge have found that in all cases where ω_0 is reliably known, it becomes larger when r_0 becomes smaller. The above new values, in the writer's opinion, are much more reasonable than the old, in view of the known great instability of the molecule, and so give support to the assumption of alternate missing lines. Furthermore, the latter assumption permits a complete explanation of the observed values of the rotational quantum number at which each branch of each band begins, in a way that was not possible with the quarter-integers. At the same time it leads to conclusions already stated as to the character (S, P, D) of the terms which are strikingly borne out by the following considerations.

Let us assume that the term xP is identical with the term $2P$ of the "main" series. This term can then be calculated from Curtis and Long's equation for the terms of this P series. (Curtis and Long's failure to observe the band $2S$–$2P$ finds explanation, as they point out, in the fact that its calculated position is at about λ 20,900.) The calculated value of the $2P$ term is 29,517.2. From this and the null-line data for the bands λ 6400 and λ 4546, the two initial S terms of these bands can then be calculated, and similarly the initial D term for the λ 5730 band. The respective null-lines of the three bands, according to Kratzer, are at 15,623.9, 21,992.8 and 17,436.6; the calculated S terms are then 13,893.3 and 7524.4, while the value of the D term is 12,080.6.

If the assumption made above as to the $2P$ term is correct, the calculated S terms should belong to a series whose first member is the common final term, here designated $2S$, of the "main" series. The series relations of the calculated term-values are perhaps most readily appreciated by giving the latter as effective quantum numbers. This is done in table 1;

TABLE 1

OBSERVED EFFECTIVE QUANTUM NUMBERS OF ELECTRONIC STATES IN HELIUM

TOTAL QU. NO.	MOLECULE, "MAIN" SERIES			ATOM, "DOUBLET" SERIES			MOLECULE, "SECOND" SERIES		ATOM, SINGLET SERIES		
	S	P	D	S	P	D	S	P	S	P	D
1									0.744		
2	1.788	(1.928)*		1.689	1.937		1.853	...	1.850	2.009	
3	**2.810**	2.928	**3.013**	2.697	2.933	2.997	...	2.964	2.857	3.011	2.998
4	**3.818**	3.928	...	3.700	3.932	3.997	...	3.965	3.858	4.011	3.998
5	...	4.928	...	4.701	4.932	4.997	...	4.966		Etc.	
6	...	5.927			Etc.			5.964			
		Etc.									

* Calculated.

the three *new* values are given in heavy type, while the remaining values are from the paper of Curtis and Long. For comparison, the effective

quantum numbers of the "doublet" and singlet terms of the helium *atom* are given. It will be seen that the calculated initial state terms for λ 6400 and λ 4546 fit perfectly as $3S$ and $4S$ into a term-series beginning with the term $2S$ of the "main" series bands. The quantum defects change somewhat more rapidly, to be sure, for these molecular S terms than for the corresponding atomic terms, but this is to be expected. Of course there is also a possibility of error in the extrapolation of Curtis and Long's formula to $2P$, but this is without doubt very small; the null-line data used also undoubtedly deviate at least slightly from the true values of the electronic term-differences. Also, it may be, in view of the writer's very

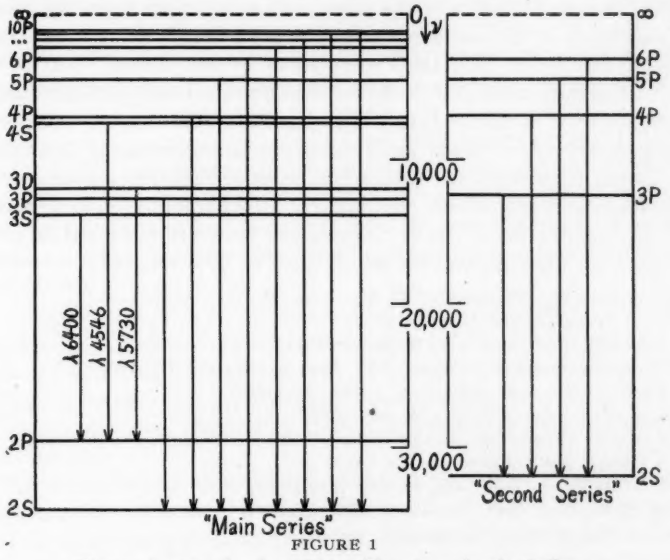

FIGURE 1

Observed energy levels and transitions in molecular helium.

strong experimental evidence[9] in favor of half-integral quantum numbers in the case of BO and in view of the recent theoretical work of Heisenberg,[10] that in the observed He_2 bands all the molecules possess $^1/_2$ quantum of vibrational energy, instead of none. This would introduce a considerable error in all the calculated electronic terms if ω_0 differed much in the different electric states of the molecule; fortunately, as is shown by the data already given, its value is fairly constant.

The calculated term-value for the initial state of λ 5730 is in accord with what might have been expected for the $3D$ term. The sub-hydrogenic character of the term—which the writer believes to be too marked to be attributed to factors already discussed which tend to produce inaccuracy in the calculated term-values—is somewhat surprising, but finds a parallel

in the case of the singlet P states of the atom. That this sub-hydrogenic character appears in the molecule for a D instead of for a P term as in the atom, may prove instructive in determining the cause of this hitherto unexplained type of deviation from the Balmer formula.

The various electron levels and transitions *now known* for the He_2 molecule are shown in the form of an energy-level diagram in figure 1.

A comparison of molecular and atomic terms, as given in the table, shows distinctly, in spite of certain irregularities, that the "main" series and related terms parallel the "doublet" terms of the atom—which presumably are really triplet terms[11]—while the "second" series terms parallel the singlet terms of the atom. These relations form the basis of the suggestion in the second paragraph as to the formation of helium molecules of two types from the two types of excited atoms. But in *both* cases, as already noted, the *molecular* terms, in the bands hitherto studied, appear to be of a singlet type. The possibility that any of these terms belong to systems of higher multiplicity can almost certainly be excluded by various considerations; this is true even though the triplet or other separations were unresolved—but appreciable separations would seem probable, at least for the $2P$ level. The future discovery of helium bands involving triplet and quintet electronic terms is, however, likely.

[1] R. S. Mulliken, *Physic. Rev.*, **25**, 290–1 and **26**, 561 (1925).
[2] R. T. Birge, *Nature*, 1926 (in press).
[3] A. Fowler, *Proc. Roy. Soc., A*, **91**, 208 (1915).
[4] W. E. Curtis and R. G. Long, *Proc. Roy. Soc., A*, **108**, 513 (1925).
[5] W. E. Curtis, *Proc. Roy. Soc., A*, **101**, 38 (1922).
[6] A. Kratzer, *Zeit. Physik.*, **16**, 353 (1923).
[7] R. Mecke, *Physik. Zeit.*, **26**, 227 (1925); cf. also *Zeit. Physik.*, **31**, 709 (1925).
[8] R. Mecke, *Zeit. Physik.*, **32**, 823 (1925).
[9] R. S. Mulliken, *Physic. Rev.*, **25**, 279 (1925).
[10] W. Heisenberg, *Zeit. Physik.*, **33**, 879 (1925).
[11] J. C. Slater, these PROCEEDINGS, Dec., 1925.

VARIATIONS IN THE PHOTO-ELECTRIC SENSITIVITY OF PLATINUM

BY LEE A. DUBRIDGE

UNIVERSITY OF WISCONSIN

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The photo-electric properties of a platinum surface which has undergone an extended process of outgassing by heat treatment have been studied by many recent observers and conflicting results have been reported.

As early as 1914 Wiedmann and Hallwachs,[1] Kustner[2] and others had found that, after prolonged heat treatment, the photo-current from a platinum surface excited by the radiation from a quartz mercury arc had decreased to values which were only a small fraction of those initially observed. This fact led these and later observers[3] to conclude that perfectly gas-free platinum would show no photo-electric sensitivity to the light ordinarily used. More recent observations, particularly those of Tucker[4] and Woodruff,[5] have shown that the decrease in the photo-electric sensitivity, which was observed, was due merely to a shift in the long wave-length limit of the specimen toward the ultra-violet to a value which might be below 1849 Å.U., the shortest line furnished by the quartz mercury arc. On the other hand the experiments of Welo[6] and, more recently, those of Herrmann[7] seem to indicate that even after prolonged outgassing a platinum surface still retains a portion of its activity to wave-lengths longer than 1849.

In view of these results it seemed worthwhile to investigate further the photo-electric properties of platinum and to see whether a condition characteristic of the gas-free metal itself could be reached. Kazda[8] has recently realized this condition with clean flowing mercury and has found a definite, long wave limit which is apparently characteristic of the metal itself.

The procedure was, in general, to heat a platinum strip in the highest attainable vacuum at various temperatures for various intervals of time with the object of determining, first, whether a definite, limiting value of the photo-current and the long wave-limit was reached and, second, how the final value was affected by various conditions of pressure and heat-treatment.

The experimental arrangement consisted merely in a narrow strip of thin platinum foil hung in the form of a loop inside a nickel receiving cylinder, the whole being enclosed in a pyrex tube which was connected through a liquid air trap to a mercury vapor diffusion pump A charcoal tube was placed near the main part of the tube to aid in attaining the lowest possible pressures. The pressure could be read on a McLeod gauge or an ionization manometer. After a thorough baking out of the entire tube at 550°C., and a long period of heating of the platinum specimen and other metal parts within the tube, the pressure reached values which were in no case greater than 5×10^{-8} mm. Hg. The platinum strip could be heated by an electric current and its temperature measured by means of an optical pyrometer. After each heating interval light from a quartz mercury arc or other source could be focussed on to the strip and the photo-current read by means of a Compton electrometer.

The results may be summarized as follows:

1. *For short heating intervals* the photo-current decreases as the tem-

perature of heating is increased, but approaches a definite limiting value *which is not zero.* The following table shows the behavior of a typical filament so treated:

TEMPERATURE °C.	HEATING TIME MINUTES	PHOTO-CURRENT CM. DEFLECTION 1 CM. = 0.3×10^{-11} AMP.
1200	0	32.3
	10	28.0
	200	26.5
1300	20	13.0
1350	15	6.2
	90	4.3
1410	20	3.5
1450	3	3.0
	150	3.0
1550	30	3.0

Several specimens were carried through their fusing point in this manner. All showed the same type of behavior, and all reached practically the same final value of the photo-electric current, though the total times of heating varied widely.

2. If the specimen is heated for *long periods of time* at a constant temperature between 1200° and 1300°C. the photo-current falls off with time of heating, but again approaches a *definite limiting value.* This limiting value is not changed by subsequently raising the heating temperature up to the fusing point, and, for a given set of incident light conditions, the value of the photo-current thus approached is practically the same as that approached in the preceding set of experiments. The following table is typical of the results obtained. The platinum specimen used in this run was cut from the same strip of foil as that used in the preceding run, and was tested in the same tube under the same pressure conditions.

HEATING TEMPERATURE 1200°C.

TIME OF HEATING HOURS	PHOTO-CURRENT CM. DEFLECTION 1 CM. = 0.3×10^{-11} AMP.
0	30.0
1	12.0
2	9.0
3	7.8
6	4.2
17	2.9
30	3.0

These values are plotted in the curve of figure 1.

In order to test whether still longer times of heating would cause a further decrease in the photo-sensitivity of the specimen a number of runs were taken in which the filament was heated for as long as 200 hours at

temperatures from 1100° to 1500°C. The general behavior was in every case the same, i.e., a final low value was reached which was not changed by further prolonged heating, or by further baking and outgassing of the tube. A typical filament is represented in the following table. Since this specimen was tested in a different tube under different incident light conditions the numerical values of the sensitivity cannot be compared with those of the previous tables. The general behavior, however, is significant.

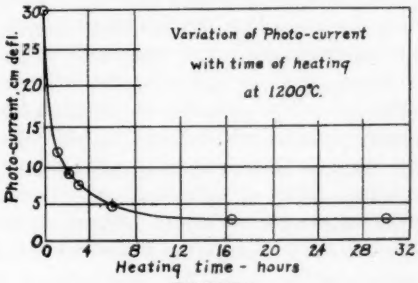

FIGURE 1

HEATING TEMPERATURE 1240°C.

TIME OF HEATING	PHOTO-CURRENT 1 CM. = 8.5×10^{-11} AMP.
0	40.0
10 min.	24.0
1 hr.	3.1
5 hr.	1.5
20	1.3
43	1.2
69	1.2
89	1.4
122	1.3

It is seen at once that during the first 20 hours of heating a low value of the sensitivity is reached which is not appreciably changed after 100 additional hours of heat treatment. This low value could not be reduced by any type of further heat treatment, no matter how high the temperature or how low the pressures. It was not reduced by surrounding the entire tube with a jacket and cooling to liquid air temperatures, nor by cooling with liquid air a mass of thoroughly baked-out charcoal which was placed in the bottom of the tube within 4 cm. of the platinum specimen itself. Cooling the tube and charcoal in this manner *did* cause the photo-sensitivity of the specimen to come *more quickly* to its equilibrium value, but the actual value reached was not changed.

These results point to the conclusion that even after prolonged heat treatment in the highest attainable vacuum a clean platinum surface is still slightly sensitive to the radiation from a quartz mercury arc, and still gives a measurable photo-electric emission.

Variation in the Long Wave Limit.—3. The outgassing of the platinum is accompanied by a shift in the long wave-length limit to a final value which is slightly above 1943 Å.U. Two methods were used to test this

conclusion. A qualitative test of the shift was made by taking simultaneous readings of the photo-electric sensitivity to the mercury arc and to a hydrogen discharge. A hydrogen tube was arranged so that the capillary through which the discharge passed was only about three cm. from the platinum strip and separated from it only by a thin fused quartz window. This furnished to the strip light of wave-lengths as short as 1800 Å.U. The intensity of the discharge was so adjusted that with the platinum in its initial state the photo-current produced by it was about the same as that produced by the arc. The following is a typical set of readings taken as outgassing progressed. In this table the initial high value of the photo-current—80 cm. deflection—is of no significance since the initial photo-currents varied widely depending upon the time of the initial baking, etc. The final values reached, however, were always nearly the same.

TIME OF HEATING	PHOTO-CURRENT		RATIO
	HG ARC	H DISCHARGE	H/HG
0	80.0	86.0	1.07
6	6.0	27.8	4.63
17	5.0	28.0	5.60
37	2.6	24.8	9.54
58	1.6	21.0	13.10
84	1.4	19.0	13.50

The large increase in the ratio H/Hg is clearly definite evidence of a shift in the photo-electric threshold to the region near where the mercury spectrum ends, but where the hydrogen spectrum is still strong, i.e., to the region just above 1849 Å.U.

A more direct test of the final limit reached was made by a method similar to that used by Williamson[9] in determining the threshold for potassium vapor. An absorption cell with fluorite windows was placed in the path of the incident light, and into this were introduced weak solutions of acetic acid in distilled water. By properly increasing the concentration of these solutions the shorter wave-length lines of the mercury spectrum could be cut out one at a time. The approximate location of the threshold was determined by introducing a solution of just sufficient concentration to cause the photo-current to disappear. A photograph was then taken of the spectrum transmitted by this solution.

When a fresh strip of platinum was tested immediately after the initial baking of the tube the threshold was found to be very close to the mercury line 2482. After prolonged outgassing, however, the photo-current was reduced to zero (i.e., to less than 0.05%) by an absorbing solution which cut out the 1943 line and all below it, leaving the 1973 still very strong. The long wave limit thus lies between these two values. This value was checked using an aluminum spark as a source.

This is higher than the threshold for outgassed platinum reported by

Tucker[4] and Woodruff[5] who find that heat treatment caused their specimens to be temporarily insensitive to wave-lengths longer than 1849. They both found, however, that this condition persisted only for a very short time—two minutes—immediately after heating and after ten minutes large photo-currents were again obtained.[10] Experiments made by the author indicate that this unstable condition is due to insufficient outgassing of the specimen. A behavior similar to that reported by Woodruff (see Fig. 4 of his paper) was observed during the *initial stages* of outgassing. After 50 hours or more of intense heat treatment, however, no such instability in the photo-sensitivity was observed and the photo-currents remained constant for hours after the heating current had been shut off. It was while the specimen was in this stable state in a pressure of the order of 10^{-8} mm. Hg that the above reported value of the threshold was observed.

Temperature Variation of Total Photo-Current.—In the results presented above, the photo-current readings were, in every case, taken after the heating current through the platinum filament had been shut off and the specimen had returned practically to room temperature. A number of tests were also made in which the photo-currents were measured while the filament was being heated by an electric current and the temperature variation of the photo-current was studied. The following results were noted:

1. During the initial stages of outgassing, the photo-currents varied widely and irregularly with the temperature of the platinum strip, as would be expected with a surface still filled with gas.

2. After prolonged heat treatment, e.g., 100 hours, the behavior became gradually more regular and ultimately settled down to a consistent variation with temperature such as is shown in the following table. These values are plotted in figure 2.

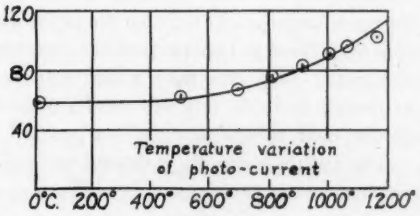

FIGURE 2

HEATING CURRENT AMPS.	FILAMENT TEMP. °C.	PHOTO-CURRENT MM. DEFLECTION
0.0	20	60
0.55	500	65
1.0	700	68
1.5	810	77
2.0	910	85
2.5	1006	92
3.0	1063	98
3.5	1150	102

Readings at higher temperatures became impossible due to the large thermionic emission. At 1150°C. the thermionic current was 50 mm. deflection; at 1063°, 3 mm.; below this, 0.

It should be pointed out that the condition of the filament at each temperature was a stable one and that the values of the photo-currents given above were each characteristic of the temperature at which they were taken, and were independent of how the temperature was reached.

There seem to be three possible explanations of such a temperature variation.

1. It is possible that at every temperature there is a characteristic equilibrium value of the gas content of the surface which gives rise to a photo-current also characteristic of that temperature. For even a "thoroughly outgassed" platinum surface is certainly far from being "gas-*free*," even though the gas-content has been reduced to the point where it no longer affects the photo-emission *at room temperature*.

2. The variation in the photo-currents observed may be due to the *heating current through* the specimen and not primarily to the temperature. Such a variation of the photoelectric emission from a Bismuth crystal whose temperature was held constant has been reported by Shenstone.[11]

3. The observed variation may be a true temperature variation caused by the increase, with rise in temperature, of the energy of the electrons within the metal, thus causing them to be more easily ejected by the incident light. That this thermal energy of the electrons within the metal becomes appreciable only at temperatures higher than about 700°C. is in line with the conclusions recently arrived at by Millikan.[12]

Further tests are now under way to determine which of the above explanations is the true one, and a more complete report will be published in the near future.

The author is greatly indebted to Prof. C. E. Mendenhall for his helpful interest in this problem.

[1] Wiedmann and Hallwachs, *Ber. Dts. Physik. Gesell.*, **16,** 107 (1914).

[2] Kustner, *Ann. Physik.*, **46,** 893 (1915).

[3] See, also, Kober and Hallvachs, *Physik. Zeit.*, **16,** 95 (1915); Sende and Simon, *Physik. Zeit.*, **21,** 562 (1920); Suhrmann, *Ann. Physik.*, **67,** 43 (1922).

[4] Tucker, *Physic. Rev.*, **22,** 574 (1923).

[5] Woodruff, *Ibid.*, **26,** 655 (1925).

[6] Welo, *Physic. Rev.*, **12,** 251 (1918); *Phil. Mag.*, **45,** 593 (1923).

[7] Herrmann, *Ann. Physik.*, **77,** 503 (1925).

[8] Kazda, *Physic. Rev.*, **26,** 643 (1925).

[9] Williamson, *Ibid.*, **21,** 107 (1923).

[10] Woodruff reports a single specimen which had a rather unaccountable abnormal behavior, becoming insensitive after heating and remaining so for two months.

[11] Shenstone, *Phil. Mag.*, **41,** 916 (1921); **45,** 918 (1923).

[12] Millikan and Eyring, *Physic. Rev.*, **27,** 51 (1926).

RADIATION AND THE DISINTEGRATION AND AGGREGATION OF ATOMS

BY G. E. M. JAUNCEY AND A. L. HUGHES

WASHINGTON UNIVERSITY, ST. LOUIS, MISSOURI

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Professor R. A. Millikan[1] has recently found evidence for the existence of very penetrating radiation which originates from sources outside of the earth. The mass-absorption coefficient of these rays is but 0.0018 per gram of water, which is far below the absorption coefficient of the hardest gamma rays. These Millikan rays are so short that their total mass-absorption coefficient is equal to the mass-scattering coefficient, the true absorption coefficient being negligible. A. H. Compton[2] gives

$$\sigma/\rho = (\sigma_0/\rho)/(1 + 2\alpha) \qquad (1)$$

where σ/ρ is the mass-scattering coefficient of X-rays of wave-length λ in a substance, σ_0/ρ is the Thomson[3] mass-scattering coefficient, and $\alpha = h/mc\lambda$, h being Planck's constant, m the mass of the electron and c the velocity of light. As σ_0/ρ is approximately 0.22 per gram for water, we find from eq. (1) that $\lambda = 0.0004$ A. However, Jauncey[4] also gives a formula

$$\sigma/\rho = (\sigma_0/\rho)/(1 + \alpha)^2 \qquad (2)$$

for the mass-scattering coefficient. Solving eq. (2) we find $\lambda = 0.0024$ A. Millikan's range of wave-lengths 0.0004 to 0.00067 A which is calculated on Compton's formula becomes 0.0024 to 0.0032 A when Jauncey's formula is used.

Millikan[1] suggests that these penetrating rays may be produced by the formation of helium out of hydrogen, or by the capture of an electron by a positive nucleus. Jeans[5] has calculated that radiation of wave-length 1.3×10^{-5} A is produced when an electron and a proton are annihilated on collision. This wave-length is calculated by equating the sum of the mass energies of the proton and electron to the energy of the quantum produced. In this calculation, however, no account is taken of the momenta before and after annihilation. Recent experiments by A. H. Compton[6] and others on the change of wave-length when X-rays are scattered and the beautiful experiments of Compton and Simon[7] on the relation between the direction of the scattered X-ray quantum and the direction of recoil of the scattering electron are only explicable on the assumption that the law of conservation of momentum holds for each individual scattering process. It, therefore, seems reasonable to require that this law should hold when radiation is produced by the destruction of matter. In this article, we shall assume

that in all interactions between radiation and matter, the following principles must be satisfied:

(*a*) Conservation of energy,
(*b*) Conservation of momentum,
(*c*) Conservation of charge,
(*d*) Reversibility of process considered,
(*e*) Velocities never to exceed that of light.

The process considered by Jeans does not satisfy either (*b*) or (*d*). The writers in a brief letter to *Nature*[8] point out that the reverse to Jeans' process would be the spontaneous disappearance of the quantum, without apparent cause and a proton and an electron to appear in its place. Such a process is difficult to imagine. We shall now proceed to discuss various processes.

1. *One Proton and One Electron.*—We shall suppose that the proton originally has a velocity $\beta_1 c$ and that the electron has a velocity $\beta_2 c$. Let the proton and electron annihilate each other, producing a quantum $h\nu$ which travels in the direction of the x-axis. Before annihilation and before coming into each other's field, let the directions of the velocities of the proton and electron make angles ϕ and θ with the x-axis. If M and m are the masses of the proton and electron, respectively, then condition (*a*) requires

$$\frac{Mc^2}{\sqrt{1-\beta_1^2}} + \frac{mc^2}{\sqrt{1-\beta_2^2}} = h\nu \qquad (3)$$

while condition (*b*) requires

$$\frac{M\beta_1 c \cos\phi}{\sqrt{1-\beta_1^2}} + \frac{m\beta_2 c \cos\theta}{\sqrt{1-\beta_2^2}} = \frac{h\nu}{c} \qquad (4)$$

and

$$\frac{M\beta_1 c \sin\phi}{\sqrt{1-\beta_1^2}} + \frac{m\beta_2 c \sin\theta}{\sqrt{1-\beta_2^2}} = 0. \qquad (5)$$

On multiplying eq. (4) by c and comparing with eq. (3), it is evident that both equations cannot be satisfied simultaneously, since $\cos\phi$ and $\cos\theta$ cannot exceed unity and β_1 and β_2 are necessarily less than unity. This process, therefore, cannot satisfy (*b*) and does not satisfy (*d*) and no radiation can be produced.

2. *One Proton and Two Electrons.*—The general case would be to have two electrons moving with different velocities in different directions and striking a proton which is also moving. This is rather complicated so we shall content ourselves with a process where one electron moving with velocity $\beta_1 c$ in a direction ϕ with the x-axis strikes another electron and proton which were originally at rest. The proton and one electron then

disappear, while a quantum $h\nu$ travelling in the direction of the x-axis appears together with the other electron moving with velocity $\beta_2 c$ in a direction θ. Condition (a) requires

$$Mc^2 + mc^2 + \frac{mc^2}{\sqrt{1-\beta_1^2}} = h\nu + \frac{mc^2}{\sqrt{1-\beta_2^2}} \tag{6}$$

while condition (b) requires

$$\frac{m\beta_1 c \cos\phi}{\sqrt{1-\beta_1^2}} = \frac{h\nu}{c} + \frac{m\beta_2 c \cos\theta}{\sqrt{1-\beta_2^2}} \tag{7}$$

and

$$\frac{m\beta_1 c \sin\phi}{\sqrt{1-\beta_1^2}} = \frac{m\beta_2 c \sin\theta}{\sqrt{1-\beta_2^2}}. \tag{8}$$

Multiplying eq. (7) by c and comparing with eq. (6), it is obvious that $\cos\theta$ must be negative and β_2 cannot be zero. The velocity of the electron which recoils after the disappearance of the proton and the other electron, therefore always has a component in the opposite direction to the direction of travel of the quantum. By differentiation it can be shown that for a given value of β_1, $h\nu$ is a minimum when $\phi = 180°$. Putting $\phi = 180°$ in eqs. (6), (7) and (8), and solving, we obtain

$$h\nu = \frac{Mc^2}{2}\left(1 + \frac{m}{M} \cdot \frac{1-\beta_1}{\sqrt{1-\beta_1^2}}\right). \tag{9}$$

The smallest value of $h\nu$ is $Mc^2/2$ when $\beta_1 = 1$, while for $\beta_1 = 0$ its value is slightly greater than $Mc^2/2$. The greatest value of $h\nu$ is ∞, which occurs when $\phi = 0°$ and $\beta_1 = 1$. Hence, this process gives $\lambda = 2.6 \times 10^{-5}$ A or less. $\lambda = 2.6 \times 10^{-5}$ A is approximately the value when two electrons and a proton fall into each other all starting from rest, in which case $\beta_2 = 0.9999995$. The reverse process of course is the quantum hitting an electron and producing a proton and two electrons. Hence all conditions are satisfied. It is curious that in the reverse process the quantum must hit a moving electron.

3. *Two Protons and One Electron.*—We shall consider only the case where two protons and one electron all originally at rest come together and produce one quantum and one proton, the momentum of the remaining proton being equal and opposite to that of the quantum. The equations are obtained from Eqs. (6) and (7) by interchanging m and M and by putting β_1 and $\phi = 0$ and $\theta = 180°$. We then obtain $h\nu = 3Mc^2/4$ (or $\lambda = 1.95 \times 10^{-5}$ A) and $\beta_2 = 3/5$. Hence conditions (a). . . .(e) are satisfied.

4. *Four Protons and Two Electrons Forming a Helium Nucleus.*—We shall consider first the case where the protons and electrons are all orig-

inally at rest. After coming together a quantum $h\nu$ is produced together with a helium nucleus recoiling in the opposite direction to that of the quantum. If M' represents the mass of the helium nucleus, then condition (a) requires that

$$(4M + 2m)c^2 = h\nu + \frac{M'c^2}{\sqrt{1-\beta^2}} \tag{10}$$

while condition (b) requires that

$$\frac{M'\beta c}{\sqrt{1-\beta^2}} = \frac{h\nu}{c} \tag{11}$$

where β is the velocity of the recoiling helium nucleus. From chemical data, we have $M + m = 1.008M_0$, $M' + 2m = 4.000M_0$ and $m = 0.0005M_0$, where M_0 is the mass of an atom of a substance of atomic weight unity. Solving (10) and (11) we obtain $h\nu = 0.031M_0c^2$ and $\beta = 0.008$. This gives a wave-length[9] of 0.00043 A, which agrees with the wave-length calculated by Millikan. The reverse process is obvious.

We may also satisfy condition (b) by assuming that the four protons and two electrons are all moving with velocity βc in the direction of the quantum which is to be ejected. The protons and electrons then come together giving rise to the quantum and a helium nucleus at rest. In this case the solution gives slightly less than 0.00043 A, while the initial velocity β is 0.008. The reverse process is a quantum hitting a helium nucleus at rest and producing 4 protons and two electrons.

Again we may satisfy condition (b) by assuming that three protons and two electrons are originally at rest while the fourth proton is moving with velocity βc in the direction in which the quantum is to be ejected. The protons and electrons come together giving rise to the quantum and a helium nucleus at rest. The solution is now λ slightly less than 0.00043 A and $\beta = 0.03$. It is interesting to consider the reverse of the three cases just discussed. It seems that a wave-length of about 0.0004 A falling on helium should break it up into hydrogen. This suggests an experiment in which two receptacles containing helium are placed the one on a mountain top so as to receive the Millikan rays and the other suspended at a depth in a mountain lake. If there is anything in the present speculations, the first receptacle after an interval of time should contain hydrogen while the second should not. Also it would seem that $\lambda = 0.0004$ A should be a critical absorption wave-length in helium. This may explain why Millikan does not find rays of wave-lengths shorter than 0.0004 A. The true mass absorption coefficient, τ/ρ, of X-rays varies approximately as $\lambda^3/\sqrt{\lambda_s^3}$ where λ_s is a critical absorption wave-length. Using the known values of τ/ρ for X-rays in aluminum and the K absorption wave-length of aluminum, we have

$$\tau/\rho = 270\ \lambda^3/\sqrt{\lambda_s^3}. \tag{12}$$

Applying this formula to absorption in helium of a wave-length just shorter than 0.0004 A, we have $\tau/\rho = 0.0017$ per gram, while Compton's formula for σ/ρ gives 0.0018 per gram, so that the total absorption coefficient μ/ρ is 0.0035 per gram. For a wave-length just above 0.0004 A, μ/ρ is 0.0018.

A fourth way of satisfying condition (*b*) is to suppose that initially we have four protons and one electron at rest and a second electron moving with velocity βc, a helium nucleus at rest and a quantum being produced. The solution of this problem gives $\lambda = 0.0008$ A and $\beta = 0.9995$. The interest in this particular process is that the inverse process is similar to the photelectric effect of X-rays in that, when a quantum of $\lambda = 0.0008$ A strikes a helium nucleus, an electron is ejected with a velocity $\beta = 0.9995$ and the remainder of the nucleus splits up into four protons and one electron. For a wave-length just shorter than 0.0008 A in helium τ/ρ is now 0.0065 per gram, making $\mu/\rho = 0.0101$ per gram if Compton's eq. (1) is used.

[1] R. A. Millikan, *Science*, Nov. 20, 1925.
[2] A. H. Compton, *Physic. Rev.*, **21**, 483 (1923).
[3] J. J. Thomson, *Conduction of Electricity through Gases*, 2nd Ed., p. 325.
[4] G. E. M. Jauncey, *Physic. Rev.*, **22**, 233 (1923).
[5] J. H. Jeans, *Nature*, Dec. 12, 1925.
[6] A. H. Compton, *Physic. Rev.*, **22**, 409 (1923).
[7] Compton and Simon, *Ibid.*, **26**, 289 (1925).
[8] Hughes and Jauncey, *Nature*, Feb. 6 (1926).
[9] In our letter to *Nature*, $\lambda = 0.0018$ A is reported instead of $\lambda = 0.00043$ A. The former is in error.

A NEW KIND OF TEST OF THE CORRESPONDENCE PRINCIPLE BASED ON THE PREDICTION OF THE ABSOLUTE INTENSITIES OF SPECTRAL LINES

BY RICHARD C. TOLMAN AND RICHARD M. BADGER

NORMAN BRIDGE LABORATORY OF PHYSICS, PASADENA

Communicated January 19, 1926

The *correspondence principle* postulates a relation between the average rate at which energy is actually being discontinuously emitted by quantum transitions and the continuous rate of emission which would be calculated on the basis of the classical theory. In the field of atomic and molecular behavior the principle has hitherto only been used to predict what spectral lines will not occur at all and to predict the *relative intensities* of spectral lines of similar origin. Since, however, the classical theory

permits a calculation of absolute rates of energy emission it should be possible to calculate from the correspondence principle the *absolute intensities* of spectral lines.

It was the purpose of the work described in this note to subject the correspondence principle to this new kind of more absolute test. Suitable data for the kind of test proposed are difficult to find owing to lack of precise knowledge of the intensities of most spectral lines, lack of knowledge of the number of atoms or molecules involved in the production of the lines and lack of knowledge as to the atomic or molecular model responsible for the lines. The recent beautiful work of Czerny,[1] however, on the spectrum of hydrogen chloride in the far infra-red provides us with at least approximate information as to the intensities of lines Nos. 8, 9 and 10 in the pure rotational spectrum of this dipole rotator, while the number of molecules involved in the production of the lines can be calculated from the Maxwell-Boltzmann distribution law as applied to rotating molecules with half quantum numbers and the measurements of Zahn[2] of the dielectric constant of hydrogen chloride gas coupled with the calculations of Pauling[3] give us the electric moment of the rotating molecules.

The results obtained can best be expressed by comparing the experimental values of Einstein's absorption coefficient B_{ij} calculated from Czerny's measurements with the theoretical values of B_{ij} calculated from the correspondence principle. For the three lines Nos. 8, 9 and 10 the calculated experimental values were 5.6, 6.8 and 10.6×10^{16} and the calculated theoretical values were 11.9, 11.8 and 11.6×10^{16}, all in c.g.s. units. For the lines in question the application of the correspondence principle treating the rotators as degenerate systems with only one quantized degree of freedom, or treating them as systems which have been made non-degenerate by spatial quantization in a weak external (magnetic) field as proposed by Kemble[4] lead to nearly the same results.

The deviations between the theoretical and experimental values of B_{ij} are possibly greater than could be accounted for by experimental error. Nevertheless, when the difficulties of the experimental work of Czerny and Zahn and the complexity of the calculations involved are considered, the approximate agreement seems satisfactory. The results considerably increase our confidence in the correspondence principle, justify us in subjecting it to further tests and lead us to hope that a precise quantitative formulation of the principle will ultimately be found.

The details of the method of calculation together with further discussion will be published in the *Physical Review*.

[1] Czerny, *Zts. Physik.*, **34**, 227 (1925).
[2] Zahn, *Physic. Rev.*, **24**, 400 (1924).
[3] Pauling, *Proc. Nat. Acad. Sci.*, **12**, 32(1926).
[4] Kemble, *Physic. Rev.*, **25**, 1 (1925).

FORMATION OF OZONE BY OPTICALLY EXCITED MERCURY VAPOR

BY ROSCOE G. DICKINSON AND MILES S. SHERRILL

GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY

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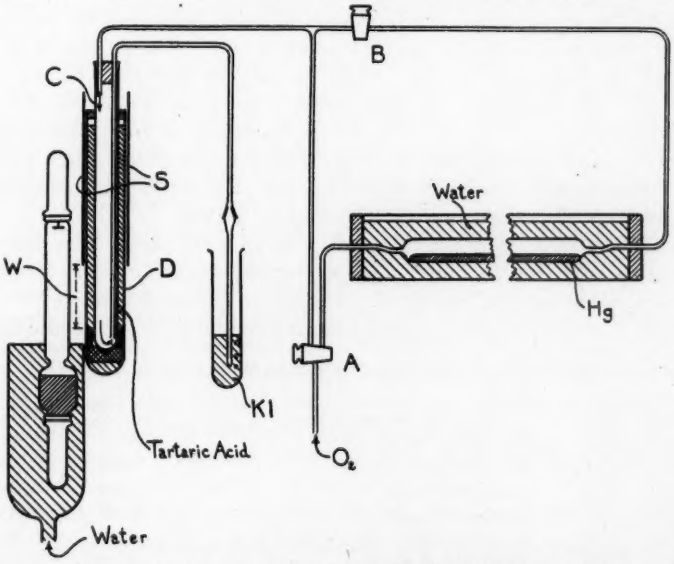
In the course of experiments[1] on the combination of hydrogen and oxygen in the presence of mercury vapor activated by absorption of the resonance radiation λ 2537 Å, it was found that the irradiation of oxygen alone in presence of mercury produced a small but still noticeable decrease of pressure. This effect might be due to ozone formation and subsequent oxidation of mercury, or to some other cause. The present experiments were accordingly undertaken to determine whether mercury vapor in the presence of its resonance radiation would cause formation of ozone.



It seemed desirable to employ a chemical method for the detection of any ozone formed. It was also important constantly to renew the traces of mercury vapor used for sensitization as fast as it became oxidized, without employing liquid mercury in the reaction tube. These conditions were met by the use of a flow method at atmospheric pressure. In order not to have the photo-sensitized reaction obscured by ordinary photo-chemical ozone formation, the radiation was filtered to remove the shortest wave-lengths from the quartz mercury-arc spectrum, since the region below 2000 Å

produces ozone[2] strongly without sensitization. These considerations led to the adoption of the following procedure.

Tank oxygen was passed through a flow meter, and over heated platinized asbestos, soda-lime and phosphorus pentoxide. It was then passed through a three-way stopcock A (see figure) into the quartz reaction tube C either directly or over a water-jacketed pool of mercury 45 cm. long. In the former case the cock B was closed. The gas issuing from the reaction tube was bubbled through 5 cc. of 2% KI solution, and this was then titrated[3] with 0.0008 normal As_2O_3 from a 2-cc. buret, using starch as indicator. With the aid of a larger quartz tube D the reaction tube was jacketed with 3 mm. of a 1.7% solution of tartaric acid to filter out short wave-lengths.[4] Since tartaric acid undergoes a slow photochemical transformation,[5] the solution was frequently renewed. The commercial lamp used was placed one centimeter from the jacket D; the lamp was water-cooled and provided with a magnet to deflect the arc against the wall adjacent to the reaction tube.

With this arrangement, no formation of ozone was observed when the oxygen was passed directly into the reaction tube. Ozone was, however, formed in appreciable amount when the oxygen had been passed over mercury. It was formed in greater amount when an opaque shield S was so interposed as to cut off part of the reaction tube from illumination. After the apparatus had been in long-continued operation, a slight yellowish brown deposit, probably mercuric oxide, was frequently observed in the reaction tube. It was easily removed by heating.

A consecutive series of typical results is given in the table. The duration of each exposure was 5 minutes. The arc current was 2.0 amperes. The temperature of the mercury was 20°C. The rate of oxygen flow was 147 cc. per minute, corresponding to an average linear velocity of 2.6 cm. per second.

EXTENT OF OZONE FORMATION UNDER VARIOUS CONDITIONS

NO.	WINDOW, W CMS.	CONDITIONS OF EXPERIMENT	CC. OF As_2O_3 REQUIRED	PARTIAL PRESSURE OZONE IN MM.
1	7.0	O_2 and Hg vapor	0.37	0.0037
2	4.0	O_2 and Hg vapor	0.92	0.0092
3	2.0	O_2 and Hg vapor	0.81	0.0081
4	1.0	O_2 and Hg vapor	0.57	0.0057
5	4.0	O_2 without Hg	0.00	0.0000
6	4.0	Duplicate of No. 2	0.85	0.0085
7	4.0	Duplicate of No. 5	0.00	0.0000
8	4.0	Duplicate of No. 2	0.90	0.0090
9	4.0	O_2 and Hg. No water or magnet on arc	0.04	0.0004
10	4.0	O_2 without Hg. No tartaric acid filter	15.30	0.1522

The results show that with the filtered radiation used, the presence of mercury vapor was essential to the ozone formation. The effect of the shield S in increasing the yield is readily explained: when a given portion of the gas is exposed long enough to the radiation, the ozone first formed oxidizes all the

mercury vapor; the remaining ozone is then photochemically decomposed. Evidence of this effect was also found by decreasing the rate of flow, which caused the *concentration* of the ozone in the issuing gas to decrease.

Since the amount of ozone formation was strongly dependent on the extent of reversal in the arc (compare Expts. 2 and 9) and since the line λ 1849 Å was absent, the first step in the sensitized ozone formation must be the excitation of a mercury atom from the normal state to the $2p_2$ state by the absorption of λ 2537 Å.

The second step in the process can hardly be the reaction: $Hg(2p_2) + O_2 = HgO + O$; for at least seven molecules of ozone were obtained per atom of mercury used. This estimate is simply the ratio of the partial pressure of the ozone to the vapor pressure of mercury, 0.0013 mm. at 20°. If the oxygen was not saturated with mercury vapor, this estimate is too low; moreover, the computed ratio is too low because both photochemical decomposition of ozone, and oxidation of mercury by ozone were neglected.

The simplest hypothesis seems to be that the second step is a collision between a mercury atom in the $2p_2$ state and an oxygen molecule, resulting in reversion of the mercury atom to the normal state and either dissociation of the oxygen molecule or production of an excited oxygen molecule. Ozone is then produced by reaction of the dissociated or excited oxygen with normal oxygen. If the collision results in dissociated oxygen the heat of dissociation of oxygen must be less than about 112,300 calories per mol, since this corresponds to the energy of the quantum λ 2537 Å. But if an excited oxygen molecule O_2' is the intermediary and ozone is produced by the reactions $O_2' + O_2 = O_3 + O$ and $O_2 + O = O_3$, then taking the heat of formation of O_3 from $\frac{3}{2} O_2$ as 34,000 calories absorbed,[6] it readily follows that the heat of dissociation of oxygen must be less than about 156,600 calories. In these calculations the kinetic energies of the colliding molecules have been neglected. Either of these results is in disagreement with the calculated value of Eucken[7] (more than 400,000 calories), but not with that of Wulf[8] (between 56,400 and 137,400 calories). It is, however, difficult rigorously to exclude possible mechanisms involving either multiple absorptions of radiation or triple collisions.

Financial assistance has been received from a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington.

Summary.—It has been shown that the photochemical formation of ozone in oxygen at atmospheric pressure by radiation from a cooled quartz mercury arc is sensitized by mercury vapor. The experiments show that activated mercury atoms can give up energy of activation to oxygen molecules instead of simply reacting with them to form oxide.

[1] Dickinson, *Proc. Nat. Acad. Sci.*, **10**, 409 (1924).

[2] Regener, *Ann. Physik.* [4], **20**, 1033 (1906).

[3] Wartenberg and Podjaski, *Zeit. anorg. allg. Chem.*, **148**, 392 (1925).

[4] Williamson (*Physic. Rev.*, **21**, 110, 1923), using a tartaric acid solution composed of 64 parts of water to 1 of saturated solution in an absorption cell 3.2 cm. in length, found no transmission below 2450 Å. Using a 3 mm. layer of 1.7% solution we found with a quartz spectrograph no transmission below 2340 Å. Moreover, through even a 0.17% solution, we obtained no unsensitized ozone formation.

[5] Kailan, *Monatshefte Chem.*, **34**, 1209 (1913).

[6] Lewis and Randall, *Thermodynamics*, McGraw-Hill Book Co., **1922**, p. 476.

[7] Eucken, *Ann. Chem.*, **440**, 111 (1924).

[8] Wulf, *J. Amer. Chem. Soc.*, **47**, 1944 (1925).

DIFFUSION OF ELECTRONS

BY GEORGE GLOCKLER*

GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY

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In order to calculate the efficiency of resonance it is necessary to know the average number of impacts Z that an electron makes in traversing a layer of gas when there is no field. The calculation of the quantity Z is given in this paper.

Method I.—Consider an element of area df in the xy plane located at the origin of a set of polar coördinates r, θ, ϕ. At a distance r from the origin there is a volume-element dV. In polar coördinates the element $dV = r^2 \sin\theta d\theta d\phi dr$. θ is the angle between the radius vector r and the z-axis. ϕ is the angle between the x, z plane and the plane containing r and z. If ρ is the number of electrons in unit-volume and N is the number of electrons that pass through a square centimeter per second, *more* in the positive than in the negative direction, then the number of such electrons that pass through the element of area df per second is [1,2]

$$Ndf = \int \frac{\rho v}{\lambda} e^{-\frac{s}{\lambda}} dV d\omega \qquad (1)$$

where v is the constant velocity of the electrons, λ is their mean free path and $d\omega$ is the solid angle subtended by df at dV. The integration is taken with respect to the total volume V. If no electric field acts then s is the radius vector r; otherwise it is the length of the parabolic path of the electrons between df and dV.

The solid angle $d\omega$ is the fraction of the surface $4\pi r^2$ which the element df subtends at dV.

$$d\omega = \frac{df \cos\theta}{4\pi r^2}.$$

Then the resultant number of electrons that pass through unit-area in one second is

$$N = \frac{v}{4\pi\lambda}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \rho e^{-\frac{r}{\lambda}} \cos\theta \sin\theta \, dr d\theta d\phi.$$

If ρ depends on z only (i.e., the case of diffusion in the z direction), we have to a first approximation

$$\rho = \rho_0\left(1 + \frac{1}{\rho_0}\frac{\partial\rho}{\partial z} r\cos\theta\right).$$

Substituting above and integrating we obtain

$$N = -\frac{v\lambda}{3}\frac{\partial\rho}{\partial z}. \qquad (2)$$

This is the equation for diffusion and the diffusion-coefficient is $D = \frac{1}{3}v\lambda$. In the present problem N is a constant and equation (2) can be integrated. We obtain

$$\rho = \frac{3N}{v\lambda}(a-z)$$

where $\rho = 0$ when $z = a$ (i.e., at the plate where the electrons are removed).

The average number of impacts that an electron makes in traversing the distance a is then

$$Z = \int_0^a \frac{v\rho}{N\lambda} dz = \frac{3}{2}\frac{a^2}{\lambda^2}.$$

This number is seen to be independent of the velocity of the electrons. Hertz[2] has derived a similar relation when the electrons are accelerated in the distance a by a small field from an initial velocity zero. His final relation for the average number of impacts in this case is $\frac{3}{4}\frac{a^2}{\lambda^2}$ instead of $\frac{3}{2}\frac{a^2}{\lambda^2}$.

Method II.—The diffusion of electrons can also be considered a "Brownian-movement" problem. The distance a tranversed by an electron is then[3]

$$a^2 = 2D\bar{t}$$

where $\bar{t}$ is the average time it takes an electron to diffuse the distance a and D is the diffusion coefficient. The average number of impacts that an electron makes in the distance a will be the average time $\bar{t}$ divided by the time τ between impacts, $\left(\tau = \frac{\lambda}{v}\right)$. That is

$$Z = \frac{\bar{t}\cdot v}{\lambda} = \frac{a^2 v}{2D\lambda}.$$

Substituting for D its value $\frac{1}{3}v\lambda$ from equation (2) we find again

$$Z = \frac{3}{2}\frac{a^2}{\lambda^2}.$$

Summary.—The average number of collisions which an electron makes when diffusing through a gas, a distance a, when no field is acting on the electron, is calculated to be $\frac{3}{2}\frac{a^2}{\lambda^2}$. λ is the mean free path of the electron. The number of impacts is seen to be independent of the velocity of the electron.

I wish to thank Professor Epstein for suggesting the second method of calculation, and also Professor Tolman for helpful criticisms.

* NATIONAL RESEARCH FELLOW IN CHEMISTRY.

[1] Riecke, *Ann. d. Phys.*, **66**, 353 (1898).
[2] Hertz, *Z. f. Phys.*, **32**, 298 (1925).
[3] Einstein, *Ann. d. Phys.*, **17**, 559 (1905).

CORRELATION BETWEEN SHAPE AND BEHAVIOR OF A CHROMOSOME

BY LILIAN V. MORGAN

DEPARTMENT OF ZOÖLOGY, COLUMBIA UNIVERSITY

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Yellow females of a race of Drosophila melanogaster, in which the two X-chromosomes are attached to each other, occasionally produce daughters that are heterozygous for yellow and for the sex-linked characters of their fathers. In this event, the daughter has received from the mother one of her two X-chromosomes detached from its mate.

In the spring of 1922, a wild type female of this kind, whose father was scute broad apricot, was mated to a forked bar male and produced, besides yellow and scute broad apricot sons, a number of forked bar sons. The forked bar males were tested in order to discover whether the mother had been an XXY female, and they proved to be sterile; they were non-disjunctional XO males. F_1 females were mated to X-ple males and gave two unexpected results; a recurrence of a number of patroclinous males and a very low number of flies of cross-over classes; among those which occurred was an unusually large proportion of double cross-overs.

Counts were then made to ascertain the percentage of crossing-over and among the flies that were examined there was a high percentage of gynandromorphs of one type. The mothers of the gynandromorphs were heterozygous for the yellow-bearing chromosome. The gynandromorphs were

zygotes that had received that chromosome from the mother and an X from the father and by elimination of the yellow chromosome had become in part male.

The low percentage and the kind of crossing-over, without doubt, and perhaps also the high non-disjunction and high percentage of gynandromorphs due to elimination of one particular chromosome, are correlated with the shape of the chromosome.

In sections of the equatorial plate of females, heterozygous for the yellow-bearing chromosome, one of the X-chromosomes, instead of being rod-shaped, is like an almost or entirely closed and somewhat rounded letter U.* Recently, homozygous females have been sectioned and, as anticipated, both X's are of this shape.

If crossing-over takes place at a time when the chromosomes are twisted about each other, the same end results that are found with two rod-shaped chromosomes will not be expected when one of them is U-shaped, hence the new cross-over ratios. The other two irregularities, high non-disjunction and frequent production of gynandromorphs, might both be expected to follow if the chromosome is slow to reach the pole of the spindle at division of the cell.

* H. J. Muller has recently reported in a paper presented before the Society of Naturalists a similar instance. Before the appearance of the female described above, he had discovered a fly which gave unusual percentages of crossing-over, and he has recently found that the shape of one X-chromosome of its heterozygous descendants is very similar to the one described here.

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*THE GENETIC BASIS OF SUSCEPTIBILITY TO TISSUE TRANSPLANTS**

BY LEONELL C. STRONG

BUSSEY INSTITUTION, HARVARD UNIVERSITY

Communicated February 4, 1926

An explanation for variation in susceptibility to transplantable neoplastic tissue has long been sought. The difficulty of throwing some light on such a complicated problem has been great. In the early years of tumor transplantation work, there was great rivalry between the upholders of the various alternative hypotheses. At the present time, we are able to reconsider the earlier work in view of recent developments and to point out some of the difficulties of the old approach.

The question whether susceptibility to a transplanted tissue is inherited or not early attracted investigators. Some said that heredity plays a part in susceptibility; others maintained the opposite view. Even with the establishment of the multiple factor hypothesis by Little and Tyzzer,

there was still skepticism expressed as to the real validity of the genetic interpretation. This interpretation which appears perfectly valid to investigators in the science of genetics, has not been fully accepted by pathologists in general. The difficulty is probably three-fold. (1) In the first place, most of the older data had been accumulated on "market mice," that is, on stocks of animals in which there had not been kept any careful breeding records of the individuals experimented upon and which undoubtedly were not uniform in genetic constitution. It is apparent, therefore, that if the phenomenon of transplantation is genetic in nature, most of these older data are worthless. However, some investigators hold fast to the old data, maintaining that no genetic phenomena are correlated with tumor susceptibility. (2) In the establishment of the multiple factor hypothesis, the process of inbreeding of stocks of mice had been employed. It is frequently maintained that this process introduces a complicating force that does not necessarily function in normal control animals. It is becoming increasingly apparent, that the process of inbreeding does not in fact introduce into a stock anything that is not already present there. On the other hand, many considerations indicate that inbreeding, as such, merely fixes in a homozygous condition specific determiners already resident in the germ plasm of the species. (3) The mathematical calculations based upon the conception of multiple mendelizing factors are somewhat involved and not fully appreciated by investigators in other fields of research. The ratios of susceptible to non-susceptible individuals in any given generation is just as clear cut, but probably not as conclusive, since enormous numbers of mice are necessary to a genetic analysis, and these numbers are usually not at hand. There is frequently heard, "Give us a 3:1 ratio so that we can understand the data, and then we will admit that susceptibility to neoplastic tissue is inherited in a mendelian manner, if it is inherited at all."

The answer to the first two of these difficulties will be evident when the genetic theory for tissue transplantation has been placed on a solid foundation. We are now able to submit data that will tend to clear up the third difficulty.

Several years ago, I started to investigate a neoplastic tissue that promised to be favorable for the answer to the third criticism above. This particular tumor had arisen in a female belonging to a relatively homozygous strain of mice. It was soon determined that all individuals belonging to this inbred strain were susceptible to the transplant. Instead of going through the period of uncertainty as was so common in tumors arising in mice from "market stock," this tumor started off by showing progressive growth in all individuals inoculated. At the same time, the same neoplastic tissue was also inoculated into individuals belonging to another inbred group of mice, not related to the first stock of mice. It was soon found that all individuals of this second stock were uniformly re-

sistant to the transplant. Thus it was demonstrated that we had two distinct stocks of individuals that differed significantly in their reactions to the same transplantable tissue. The F_1 individuals, produced by crossing individuals belonging to these two original stocks of mice, were all susceptible and all grew the transplant progressively. In the F_2 generation, two classes of individuals were demonstrated. These two classes were present in the ratio of 9 susceptible to 7 non-susceptible individuals. The data were analyzed genetically. It is apparent that we were dealing with multiple factors. Furthermore, the number of these genetic factors involved in susceptibility to neoplastic tissue is probably two. We concluded from these data, and other data accumulated since that time, that for the successful growth of the transplant, there must be the simultaneous presence of two independently segregating factors in the fundamental makeup of the host, that are derived from the zygote from which the host had developed. These data indicated the smallest number of genetic factors involved in differentiating susceptible from non-susceptible individuals. In order, however, to further demonstrate that the phenomenon of transplantation was really genetic, further work was undertaken to separate these two mendelian factors. This of course appeared to be only a matter of time, since the data upon which the evidence rested, indicated that the two mendelian factors were segregating independently of each other.

In order to accomplish this end, seven groups of F_2 litters were isolated. All individuals were inoculated with the transplant. Those individuals that proved to be susceptible to the transplant, were subjected to operation. The mass was excised as carefully as possible under general anesthesia. The number of individuals showing recurrent masses after operation gradually grew less as the technique of removing the entire transplant became perfected. Some of the subfamilies are not included in this paper since they showed nothing of importance for the present analysis. The data for certain generations submitted are quite meager in several cases. This meagerness of data, however, is usually confined to the earlier generations before proper technique for the complete removal of the transplant had been perfected. In other cases, the small numbers occurred in certain generations in which there was nothing of importance apparent, so that the parents producing these generations were killed off in order to make room for the more important subfamilies. The data for two of these special families (E-I and E-VII) are given in table one.

Table one gives the data obtained for the several successive generations of individuals used in the experiment. The term + means a susceptible animal; the term − means a non-susceptible or resistant individual; $-\times+$ means that a non-susceptible individual was mated to a susceptible individual.

There are three features of the present data that call for discussion: (*A*) In the F_3 generation of the E-I family a high percentage of negative

TABLE 1

E-I FAMILY

	a TOTAL +	−	PE	PER CENT NEGATIVES	*b* + × + +	−	PE	PER CENT NEGATIVES
F_3	24	37	±2.54	60.66%±4.16	13	4	±1.17	23.53%± 6.88
F_4	51	35	±3.03	40.69%±3.53	17	8	±1.55	32.00%± 6.20
F_5	21	48	±2.55	69.56%±3.70	6	2	±0.81	25.00%±10.15
F_6	0	84		100.00%				

	c − × + +	−	PE	PER CENT NEGATIVES	*d* − × − +	−	PE	PER CENT NEGATIVES
F_3	7	6	±1.20	46.15%±9.21	4	27	±1.24	87.09%±4.00
F_4	34	22	±2.43	39.28%±4.34	0	5		100.00%
F_5	15	9	±1.58	37.50%±6.58	0	37		100.00%
F_6					0	84		100.00%

E-VII FAMILY

	e TOTAL +	−	PE	PER CENT NEGATIVES	*f* TOTAL + × + +	−	PE	PER CENT NEGATIVES
F_3	41	26	±2.65	38.80%±3.96	41	26	±2.65	38.80%±3.96
F_4	139	43	±3.62	23.62%±1.99	130	38	±3.61	22.62%±2.15
F_5	90	27	±3.03	23.08%±2.58	81	26	±2.95	24.29%±2.76
F_6	75	25	±2.88	25.00%±2.88	67	20	±2.61	22.99%±3.00
F_7	103	38	±3.51	26.95%±2.49	74	21	±1.79	22.11%±1.88
F_8	90	0		0.00%	90	0		0.00%

	g TOTAL +	− × + −	PE	PER CENT NEGATIVES	*i* SOME NEGATIVES IN LITTERS +	− × + −	PE	PER CENT NEGATIVES
F_3								
F_4	9	5	±1.19	35.72%±8.49	9	5	±1.19	35.72%± 8.49
F_5	9	1	±0.66	10.00%±6.66	3	1	±0.57	25.00%±14.25
F_6	8	5	±1.17	38.46%±9.00	8	5	±1.17	38.46%± 9.00
F_7	29	17	±2.18	36.95%±4.74	15	17	±1.88	53.12%± 2.43

	j SOME NEGATIVES IN LITTERS +	+ × + −	PE	PER CENT NEGATIVES	*k* NO NEGATIVES IN LITTERS +	+ × + −	PER CENT NEGATIVES
F_3	23	9	±1.69	28.12%±5.28	8	0	0.00%
F_4	94	38	±3.46	28.98%±2.43	36	0	0.00%
F_5	70	26	±2.90	27.08%±3.02	11	0	0.00%
F_6	52	20	±2.53	27.77%±3.52	15	0	0.00%
F_7	56	21	±2.60	27.27%±3.06	18	0	0.00%
F_8					90	0	0.00%

Grand Total:
634 + : 363 — ±10.15 or 36.41% ± 1.01.

individuals was obtained. This suggested that an approach could be made toward the original non-susceptible genetic complex by continued mating from these negative individuals. Consequently, a selection series toward low susceptibility was started. The data obtained are given in column *d* of the E-I family. Resistance to the transplant increased from 87.09%

in the F_3 generation to 100.00% in the F_4, and continued at that point for the next two generations. F_6 individuals were then crossed to the original non-susceptible stock of mice and no evidence could be obtained that the F_6 non-susceptible individuals differed in any respect in their reactions to the transplanted tissue than the original non-susceptible stock individuals. We had consequently recombined the genetic complex of the original non-susceptible parent by continued breeding, after the original combination of non-susceptibility factors had been introduced only once into the hybrid (in the formation of the F_1 generation).

(*B*) Column *k* of the E-VII family gives data also of significant nature. A selection experiment was started in the opposite direction, that is, toward high susceptibility. This experiment had to be performed several times and only the data showing a positive effect of selection are included. This result was to be expected, since the two susceptibility factors had been demonstrated to be dominant over the factors for non-susceptibility. It is readily apparent that a synthetic stock of mice had been developed through the process of selection, all individuals of which are susceptible to the transplant. We had consequently recombined the genetic factors underlying the reaction of the original susceptible individuals after the original combination of susceptibility factors had been introduced into the experiment only once (in the formation of the F_1 generation).

These two selection lines (E-I *d* and E-VII *k*) demonstrate that we are dealing with specific determiners of susceptibility and non-susceptibility. Furthermore, that these genetic factors underlying susceptibility to tissue transplants are not unique but belong to the same general class of all other fully recognized mendelian units or factors (genes).

In order to demonstrate even more clearly that specific genetic factors are concerned in tissue susceptibility, one further series of experiments was undertaken.

By inspection of several relatively large groups of F_3 individuals, produced by mating several pairs of susceptible F_2 individuals together, we were able to pick out a few groups in which the number of negative individuals appeared to be about twenty-five per cent of the total. Since this is the per cent of negative individuals expected when only one mendelian dominant factor is alone segregating, it was more than probable that of the two susceptibility factors entering into the original experiment, one had probably got into the homozygous condition by being passed through an individual of the F_2 generation, thus giving no evident sign of further disjunction. One of the selection lines is given in column *j* of the E-VII family. The side branches of this family in which all the offspring proved to be susceptible to the transplant were discarded. I purposely tried, therefore, to keep this apparent single dominant susceptibility factor in

the heterozygous condition for five generations. In these five successive generations, 409 individuals were produced (in this main selection series), 295 of these proved to be susceptible to the transplant, while 114 failed to grow the same tissue. The ratio obtained (295+ : 114− ± 6.04 or 27.87% ±1.45) is practically indistinguishable from a 3:1 ratio, expected in the offspring produced by mating together two individuals heterozygous for a single dominant gene. (3:1 ratio for this number of individuals = 306.75 + : 102.25− ±4.99 or 25.00% ±1.22.) The deviation from the expected 3:1 ratio is 27.87% ±1.45−25.00% ±1.22 or 1.87% ±1.84 = 1.016 times the probable error.

Negative individuals of the F_7 generation were then backcrossed to the original susceptible stock of mice. It was found that all the F_1 individuals produced were susceptible as the original F_1 individuals in the first original cross had been. Then by raising a new F_2 generation from this cross two classes of individuals were obtained. Out of a total number of 368 individuals obtained, 270 proved to be susceptible to the transplant and 98 were non-susceptible. (270+ : 98− ±5.65 or 26.63% ±1.53.) On an expected 3:1 ratio for this number of individuals, the number of susceptible to non-susceptible individuals ought to be 276+ : 92− ±5.57 or 25.00% ±1.51. This observed ratio in the F_2 generation is not significantly different from the 3:1 ratio, the deviation from expectation being 26.63% ±1.53−25.00% ±1.51 or 1.63% ±2.14 = 0.76 time the probable error. There is, therefore, demonstrated that a single dominant mendelian factor is producing the phenomenon of the reactivity of the host to neoplastic tissues. This reduces the number of variable factors underlying susceptibility to transplanted tumors to lowest terms.

The data at hand demonstrate very conclusively the mechanism of susceptibility to tissue transplants. It is in the germ plasm of the host that we are to look for this causal determiner. The problem of tissue transplantation thus becomes a specific problem for the science of genetics. Whether the method developed in these experiments will solve only a part of the problem of tissue transplantation or whether similar experiments will lead to a further investigation of the cancer situation remains to be demonstrated. Experiments are now under way to determine the intrinsic factors within the tumor cell that determine its physiological activity.

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ON VARIOUS GEOMETRIES GIVING A UNIFIED ELECTRIC AND GRAVITATIONAL THEORY

BY JOSEPH MILLER THOMAS*

PRINCETON UNIVERSITY

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1. Recently Einstein[1] has deduced a unified theory of electric and gravitational fields by forming the Euler equations for the integral of a certain scalar density. I show in the present paper that his new equations can be obtained by direct generalization of the equations of the gravitational field previously given by him. The process of generalization consists in abandoning assumptions of symmetry and in adopting a definition of covariant differentiation which is not the usual one, but which reduces to the usual one in case the connection is symmetric.

In the final section I show that the adoption of the ordinary definition of covariant differentiation leads to a geometry which includes as a special case that proposed by Weyl[2] as a basis for the electric theory; further, that the asymmetric connection for this special case is of the type adopted by Schouten[3] for the geometry at the basis of his electric theory.

2. Einstein's equations for the simple gravitational field are

$$g_{ij,k} = 0, \tag{2.1}$$

$$R_{ij} = 0. \tag{2.2}$$

They involve a fundamental (metric) tensor g_{ij} and an affine connection Γ^k_{ij}, both of which are symmetric in i and j. The symbol $g_{ij,k}$ denotes the covariant derivative of g_{ij},

$$g_{ij,k} = \frac{\partial g_{ij}}{\partial x^k} - g_{\alpha j}\,\Gamma^\alpha_{ik} - g_{i\alpha}\,\Gamma^\alpha_{jk}, \tag{2.3}$$

and R_{ij} denotes the Ricci tensor formed for the Γ's.

Let us now consider an asymmetric connection H^i_{jk} and an asymmetric tensor h_{ij}, setting

$$H^i_{jk} = \Gamma^i_{jk} + \Omega^i_{jk}, \tag{2.4}$$

$$h_{ij} = g_{ij} + \omega_{ij}, \tag{2.5}$$

where Γ^i_{jk} and g_{ij} indicate the symmetric parts, and Ω^i_{jk} and ω_{ij}, the skew symmetric. If we now postulate that the general equations of the gravitational and electric field are those obtained by abandoning the assumptions of symmetry in (2.1) and (2.2), we get

$$h_{ij/k} = 0, \tag{2.6}$$

$$Z_{ij} = 0, \tag{2.7}$$

where

$$Z^i_{jkl} = \frac{\partial H^i_{jk}}{\partial x^l} - \frac{\partial H^i_{jl}}{\partial x^k} + H^\alpha_{jk} H^i_{\alpha l} - H^\alpha_{jl} H^i_{\alpha k},$$

and

$$Z_{ij} = Z^\alpha_{ij\alpha}$$

are the natural generalizations of the curvature and Ricci tensors, respectively.

We have yet to define the symbol appearing in (2.6) by choosing a generalization of the covariant derivative appearing in (2.1). If we write

$$h_{ij/k} = \frac{\partial h_{ij}}{\partial x^k} - h_{\alpha j} H^\alpha_{ik} - h_{i\alpha} H^\alpha_{kj}, \tag{2.8}$$

then (2.6) and (2.7) are the equations which Einstein gets after assuming

$$\Omega^\alpha_{\alpha k} = 0 \tag{2.9}$$

in order to make his equations agree with experimental facts.[4] In the present mode of deduction no such additional assumption is necessary. The geometrical significance of conditions (2.9) is indicated in the next section.

3. It can be shown[5] that if we transform the connection H^i_{jk} by the formulas

$$H^i_{jk} = H'^i_{jk} + 2\delta^i_j v_k, \tag{3.1}$$

where v_k is an arbitrary vector, that infinitesimal parallelism (and consequently paths) will be preserved in the sense that the direction of the vector obtained by displacement of a given vector through dx is the same for the laws of displacement determined by the two sets of H's.

Under a transformation such as (3.1) we have also

$$\Omega^i_{jk} = \Omega'^i_{jk} + \delta^i_j v_k - \delta^i_k v_j. \tag{3.2}$$

Hence it is seen that by choosing v_j properly we can realize conditions (2.9) with preservation of displaced directions.

Defining $h_{ij/k}$ by (2.8), we can write the Einstein equations corresponding to (2.6) as

$$h_{ij/k} = h_{ij}\varphi_k + h_{ik}\varphi_j,$$
$$\varphi_k = -\frac{2}{n-1}\Omega^\alpha_{\alpha k}. \tag{3.3}$$

These are, of course, his equations before assumption (2.9) is made. It is easily shown that equations (3.3) are invariant under the transformation (3.1), whereas the equations (2.7) are not.

As a consequence of (3.3), we have on taking $\varphi_i = 0$, and on using (2.4) and (2.5)

$$g_{ij,k} = \omega_{\sigma j}\,\Omega^{\sigma}_{ik} + \omega_{i\sigma}\,\Omega^{\sigma}_{kj}.$$

From these last equations it follows that

$$g_{ij,k} + g_{jk,i} + g_{ki,j} = 0. \tag{3.4}$$

Since the imposing of conditions (2.9) does not affect the geodesics, we can state[6] the

THEOREM. *The equations of the paths (straightest lines) of Einstein's space have a homogeneous quadratic first integral whose coefficients are the components of the symmetric part of the fundamental tensor.*

4. The covariant derivative defined by (2.8) can be extended in a number of ways to tensors of any rank. One such way is the following. The term to be subtracted corresponding to a covariant index p is of the form $h_{i\ldots\alpha\ldots j}\,H^{\alpha}_{pk}$ or of the form $h_{i\ldots\alpha\ldots j}\,H^{\alpha}_{kp}$ according as p occupies an odd or even position among the subscripts of h counting from the left. It is readily shown that the resulting expressions are the components of a tensor.[7]

This definition, however, is not the one usually adopted.[8] If applied to the product of two vectors $\varphi_i\psi_j$, the result is *not* $\varphi_i\psi_{j/k} + \varphi_{i/k}\psi_j$ as is the case with ordinary covariant differentiation.

5. We shall next derive a few properties of fundamental tensors satisfying

$$h_{ij;k} = 0, \tag{5.1}$$

where

$$h_{ij;k} = \frac{\partial h_{ij}}{\partial x^k} - h_{\alpha j}\,H^{\alpha}_{ik} - h_{i\alpha}\,H^{\alpha}_{jk}$$

is the ordinary covariant derivative of h_{ij} with respect to the connection H. Equations (5.1) are equivalent to the two sets $g_{ij;k} = 0$ and $\omega_{ij;k} = 0$, the first of which can be written as

$$g_{ij,k} = g_{\alpha j}\,\Omega^{\alpha}_{ik} + g_{i\alpha}\,\Omega^{\alpha}_{jk}, \tag{5.2}$$

where $g_{ij,k}$ is defined by (2.3).

From (5.2) it follows that equations (3.4) are fulfilled in this case also.[9] The tensor g_{ij}, therefore, furnishes a quadratic first integral for the equations of the paths just as in the case of Einstein's space.

The conditions that such a tensor give a Weyl metric geometry for some affine connection with the same paths have been given previously.[10] They are

$$2(n-1)g_{ij,k} + g^{\alpha\beta}(g_{jk}\,g_{\alpha\beta,i} + g_{ik}\,g_{\alpha\beta,j} - 2g_{ij}\,g_{\alpha\beta,k}) = 0. \tag{5.3}$$

From (5.2) we get

$$g^{\alpha\beta}\, g_{\alpha\beta,k} = 2\Omega^{\alpha}_{\alpha k}. \tag{5.4}$$

Substituting from (5.2) and (5.4) in (5.3) we find that equations (5.3) are here equivalent to

$$\Omega^{i}_{jk} - \frac{\delta^{i}_{j}}{n-1}\,\Omega^{\alpha}_{\alpha k} + \frac{\delta^{i}_{k}}{n-1}\,\Omega^{\alpha}_{\alpha j} = 0.$$

These conditions show that the connection is of the semi-symmetric type employed by Schouten in his electrical theory.[11]

If in (3.1) we chose $v_k = \Omega^{\alpha}_{\alpha k}/(n-1)$, by means of (3.2) we see that Schouten's connection is rendered symmetric with preservation of displaced directions (parallelism).[12] This transformation changes equations (5.3) into

$$(g_{ij,k})' = 4g_{ij}\,\Omega^{\alpha}_{\alpha k}/(n-1),$$

the covariant derivative being formed with respect to Γ'. Written in the form $(g_{ij,k})' = -\,g_{ij}\,\psi_k$, these equations put in evidence the Weyl character of the geometry and show that the symmetric connection associated with Schouten's geometry is the affine connection of Weyl's.[13]

The geometries of Schouten and Weyl which enter here as particular cases of the geometry characterized by (5.1) are therefore equivalent. If we look upon (5.1), or (5.2), both as a means of rendering Schouten's geometry metric and of determining an asymmetric part for Weyl's symmetric affine connection, then we can say that the metric geometries of Schouten and Weyl are equivalent. It is to be noted, however, that an asymmetric part can be obtained from (5.2) for an arbitrary Weyl geometry, whereas the general Schouten geometry will not admit a fundamental tensor satisfying (5.2).

* NATIONAL RESEARCH FELLOW IN MATHEMATICS.

[1] *Berliner Sitzungsberichte*, **1925**, pp. 414–419.

[2] *Raum, Zeit, Materie*, 4th ed., p. 109, et seq.

[3] *Proceedings, Amsterdam Academy*, Vol. 26, 1923, p. 850.

[4] Einstein assumes (2.9) to make the right hand member of (3.3) vanish. He does not use the conditions in any other connection in the cited paper.

[5] H. Friesecke, *Math. Annalen*, Vol. 94, 1925, p. 106.

[6] Cf. Veblen and T. Y. Thomas, *Trans. Amer. Math. Soc.*, Vol. 25, 1923, p. 581, for the theorem (first proved for the Riemann geometry by Ricci and Levi-Civita) that (3.4) are the conditions for a quadratic first integral.

[7] A simple method of proof, suggested by Professor Veblen, is the following. Subtract the expression defined above from the ordinary expression for the covariant derivative, which is known to be a tensor. The resulting difference is readily recognized as a tensor because of the tensor character of the skew symmetric part of the connection.

[8] Cf. Schouten, *Ricci-Kalkül*, pp. 63–65.

[9] I am indebted to Professor Veblen for this remark.

[10] Cf. my paper "First Integrals in the Geometry of Paths," in these PROCEEDINGS, **12**.

[11] Loc. cit.

[12] In a paper entitled "Asymmetric Displacement of a Vector" to appear in the *Transactions of the American Mathematical Society* I have established this and other properties of the semi-symmetric connection, together with properties of the general asymmetric connection.

[13] Schouten in his *Ricci-Kalkül*, p. 223, remarks that his geometry of the semi-symmetric connection and that of Weyl have the same paths. He further states that it is impossible to transform his asymmetric connection into Weyl's symmetric connection by a transformation preserving paths (bahntreue Transformation) because an asymmetric connection remains asymmetric under such a transformation. The latter statement, however, is true only as a consequence of his definition of a "bahntreue Transformation" (loc. cit., p. 76) in which he makes the unnecessary assumption that the change of the skew symmetric part is zero. When one asks what change of connection preserves *all* displaced directions, one finds that the change affects both the symmetric and skew symmetric parts of the connection, and that the change in the symmetric part not only preserves the paths, but is the most general change that does. See my paper cited under note 12.

STUDIES ON BIOCHEMICAL DIFFERENCES BETWEEN (+) AND (−) SEXES IN MUCORS. 2. A PRELIMINARY REPORT ON THE MANOILOV REACTION AND OTHER TESTS[1]

BY SOPHIA SATINA AND A. F. BLAKESLEE

STATION FOR EXPERIMENTAL EVOLUTION, COLD SPRING HARBOR, N. Y.

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Since 1913,[2] attempts have been made in this laboratory to discover biochemical differences which it was believed must exist between the opposite sexes in the group of fungi known as Mucors. That chemical methods are capable of distinguishing races which appear identical morphologically has been shown in the case of the yellow-coned races of Rudbeckia.[3] As outlined in our paper of last year,[4] it has been our purpose to run through a series of easily applied tests on a series of representative sexual races before undertaking an intensive study of any single biochemical reaction. While this program was underway, our attention was called to the reaction of Manoilov[5] for the identification of sexes which we have tested with a relatively large number of Mucors as well as of green plants. On account of a lack of any constant morphological difference in Mucors, which would enable one to determine which is male and which female, we have provisionally designated the opposite sexes by the signs (+) and (−). The Mucors reproduce chiefly by means of non-sexual spores. The various races, therefore, may be kept pure under cultivation without change of sex through vegetative reproduction.

In all cases the Mucors were grown on our nutrient number 230 for about 8–9 days when weighed amounts of the fresh mycelium were extracted with 60 per cent alcohol or after grinding extracted with distilled water and cleared by centrifuging. The various races of a given species were generally handled in pairs so that a (+) was always compared with a (−).

Table 1 shows the results of tests with five pairs of races of Mucor IV. In this, as in other tables, the strengths of reaction are graded A to D when a more quantitative expression of the differences was not possible. In addition to averages, the races are grouped according to the number of (+) and (−) races among the stronger and weaker members of the pairs.

TABLE 1

BIOCHEMICAL TESTS WITH MUCOR IV

PAIR NO.		I	II	III	IV	V	STRONGER REACTION	WEAKER REACTION	AVERAGE
Peroxidase	(+)	D	D+	D+	B−	C−	2	3	C−
	(−)	D+	C	C	C	D+	3	2	C
Catalase	(+)	19.0	17.0	5.0	10.5	3.5	3	2	11
	(−)	14.0	3.5	4.0	14.0	4.5	2	3	8
Reduction	(+)	7	9	7	6	6	4	1	7
	(−)	9	7	9	10	10	1	4	9
Total Acidity	(+)	C	A−	A	A−	A	4	1	B+
	(−)	C+	B	C+	B	B	1	4	B−
pH (w. extr.)	(+)	5.0	5.1	5.1	6.1	6.1	3	2	5.48
	(−)	5.1	4.9	4.9	6.2	6.2	2	3	5.46
pH (in medium)	(+)	4.2	4.2	4.1	4.0	4.1	3	1	4.12
	(−)	4.3	4.1	4.1	4.2	4.2	1	3	4.18
pH (alc. extr.)	(+)	4.8	5.0	5.0	4.7	4.8	3	2	4.86
	(−)	5.0	4.7	4.9	5.0	4.9	2	3	4.90
Manoilov reaction	(+)	B	C+	D	A	B	4	1	C+
	(−)	D	D	C−	D	D	1	4	D+

Water extracts were tested for *oxidases*. No *oxigenase* could be demonstrated in this or in other Mucor species by the indophenol reaction when tests were made with α-naphthol and dimethyl-*p*-phenylene-diamine. *Peroxidase* was evident in all cases when tested by the above reagents plus H_2O_2. *Tyrosinase* could not be demonstrated when tested with tyrosin in this nor in other species of Mucors. *Catalase* was present in larger average amounts in the (+) than in the (−) races. The figures indicate the amount of gas given off after 30 minutes in the Bunzel apparatus by 1 cc. of H_2O_2 per 1 cc. of extract which had been neutralized with $CaCO_3$.

For the *Reduction Reaction* the figures indicate the number of drops of water extract necessary to reduce 3 cc. of $0.002/N$ $KMnO_4$. The lower numbers, therefore, indicate the stronger reducers. In all the pairs, with one exception (Pair I) the (+) shows a stronger power of reduction than the (−) race.

Total Acidity of water extract was tested by titration with $N/10$ KOH phenolphthalein being used as indicator. Equal numbers of drops of the KOH were taken in each case and the relative acidity was roughly determined by the color reaction. The water extracts average more acid in the (+) races.

The pH of the water extract, of the medium in which the moulds have grown, and of the alcoholic extract, determined by the colorimetric method, show little difference between (+) and (−).

With the *Manoilov reaction*, used with alcoholic extracts, the (+) races show the higher grades or a female reaction, except in Pair III.

Table 2 gives the results of testing, with the Manoilov reaction, 108 sexual races included in 18 species and 8 genera. In only 6 races were there incorrect determinations. These 6 races have been repeatedly retested and shown to be true reversals. More concerning the Manoilov reaction will be given in the paper which follows.

TABLE 2

IDENTIFICATION OF SEX IN MUCORS BY MANOILOV'S REACTION

SPECIES	NUMBER OF RACES	(+)	(−)	CORRECT IDENTIFICATION	INCORRECT IDENTIFICATION
Phycomyces	2	1	1	2	.
Rhizopus nigricans	39	19	20	37	2 (−)
Syncephalastrum	2	1	1	2	.
Cunningh. Bertholl.	10	5	5	9	1 (−)
Circinella spinosa	2	1	1	2	.
C. umbellata	2	1	1	2	.
Absidia glauca	9	4	5	7	2 (+)
A. Blakesleeana	13	7	6	13	.
Parasitella	5	1	4	5	.
Mucor Mucedo	2	1	1	2	.
Mucor griseocyanus	2	1	1	2	.
Mucor hiemalis	1	..	1	1	.
Mucor D	2	1	1	2	.
Mucor N	2	1	1	2	.
Mucor IV	10	5	5	9	1 (+)
Mucor V	2	1	1	2	.
Mucor VII	2	1	1	2	.
Mucor H	1	1	..	1	.
Total	108	52	56	102	6

94.5% correct identifications; 5.5% incorrect identifications.

In table 3 are shown tests for catalase in 45 races of Mucors included in 12 species and 7 genera made in the Bunzel apparatus. With only one exception, the (+) races in each species showed a larger average catalase content than the (−). Exceptions do occur within the different species, but there are roughly 3 times as many (+) races among those with stronger

catalase reaction and 3 times as many (−) races among those with weaker reaction.

TABLE 3

TESTS OF CATALASE IN MUCORS

SPECIES	STRONGER REACTION (+)	STRONGER REACTION (−)	WEAKER REACTION (+)	WEAKER REACTION (−)	TOTAL NO. OF RACES (+)	TOTAL NO. OF RACES (−)	AVERAGE VOL. OF O_2 PER 1 CC. OF EXTRACT (+)	AVERAGE VOL. OF O_2 PER 1 CC. OF EXTRACT (−)
Phycomyces	1	0	0	1	1	1	12.7	8.8
Rhizopus nigricans	2	1	1	2	3	3	11.1	10.0
Syncephalastrum	1	0	0	1	1	1	17.0	16.0
Circinella umbellata	1	0	0	1	1	1	9.3	3.2
Absidia glauca	3	2	1	3	4	5	14.2	13.6
Parasitella simplex	1	0	0	3	1	3	15.5	5.9
Mucor griseocyanus	0	1	1	0	1	1	5.7	15.0
Mucor D	1	0	0	1	1	1	7.2	4.2
Mucor N	1	0	0	1	1	1	2.8	2.0
Mucor IV	3	2	2	3	5	5	11.0	8.0
Mucor V	1	0	0	1	1	1	8.2	3.2
Mucor VII	1	0	0	1	1	1	13.8	10.7
Total	16	6	5	18	21	24	10.7	8.4

In table 4 is given a summary of various tests with the species listed in table 3 (with addition of Cunninghamella Bertholletiae). All the races were included which showed reversals in the Manoilov reaction and as a consequence this reaction gives a poor average in the few races of Rhizopus tested. In the last column are given for the races involved, the average grade showing the reduction of tellurium.[4] From table 4 it seems evident that there is a significant average difference between the (+) and (−) races as shown by the Manoilov reaction, the greater catalase content of the (+), the greater reduction of $KMnO_4$ by (+) extracts and the greater reduction of tellurium in living cells of (+) races. In addition, both the total acidity of the water extracts and the peroxidase content average slightly greater for the (+) races. The pH differences between races in the water and alcoholic extracts as well as in the medium cannot be seen to have any relation to sex.

Among other tests which failed to show any significant difference between the sexes are vital stains (22 different aniline dyes, including both acid and basic types, used with 30 races) and combinations of Mucors (20 races) in cultures with chromogenic bacteria (11 races) (methods of Matruchot and Nadson). The method of Karczag[6] gives promise of being a valuable test.

Microchemical Tests.—By the indicator method, the conjugating filaments were investigated for pH in 80 "contrasts" between (+) and (−) sexes using 64 different races (in 11 species and 7 genera) of heterothallic Mucors and 8 races (7 species in 5 genera) of the homothallic group. In

every case the opposite gametes (coenogametes) showed a distinct difference in pH (such as between about 4.8 and 4.0) although in most cases it was not possible without special technique, to determine which was connected with the (+) and which with the (−) mycelium. In 7 pairs of gametes in Mucor Mucedo, however, it was found that the (+) gamete had the higher pH value and in 29 pairs of Phycomyces, 17 (+) gametes and 12 (−) gametes had the higher pH. In homothallic species usually, but not always, the larger gamete has the higher pH value. The gametes

TABLE 4

SUMMARY OF BIOCHEMICAL TESTS WITH MUCORS

SP.	SEX	NOS.	pH ALC. EXTR.	MAN.	pH IN MED.	pH H_2O EXTR.	ACIDITY	PEROX.	CATALASE	REDCT. EXTR.	REDCT. CELLS
Ph.	(+)	1	6.20	A	4.75	6.15	A	B	12.7	2.0	..
Ph.	(−)	1	6.20	C	4.80	6.20	C	C+	8.8	3.0	..
Rh.	(+)	3	..	C+	2.87	5.60	C	C+	11.1	3.7	..
Rh.	(−)	3	..	C+	2.96	5.59	C	C−	10.0	4.0	..
Syn.	(+)	1	..	A	3.55	5.78	C	O	17.0	8.0	90.0
Syn.	(−)	1	..	C	3.45	5.82	B	O	16.0	8.0	90.0
Cun.	(+)	5	5.99	C+	3.73	6.47	B−	C+	..	4.6	84.6
Cun.	(−)	5	5.97	D	3.81	6.45	C+	C	..	5.0	82.0
Cir.	(+)	1	6.05	B	4.50	6.20	B	B	9.3	9.0	88.0
Cir.	(−)	1	5.95	D	4.60	6.10	C	D	3.2	7.0	67.0
A. gl.	(+)	4	4.61	C+	3.37	6.10	B+	B−	14.2	8.8	82.5
A. gl.	(−)	5	4.76	D	3.45	6.28	B−	C	13.6	8.6	76.2
Par.	(+)	1	4.60	B	4.10	5.85	A	C+	15.5	7.0	..
Par.	(−)	3	4.68	D+	4.15	5.77	B−	C	5.9	11.0	..
M. gr.	(+)	1	6.00	A	3.41	6.20	C	C	5.7	7.0	90.0
M. gr.	(−)	1	6.10	D	3.52	6.25	C	C+	15.0	8.0	80.0
M. D.	(+)	1	4.60	C	4.05	5.20	A	C	7.2	5.0	89.0
M. D.	(−)	1	4.60	D	4.10	4.40	C	D	4.2	7.0	81.0
M. N.	(+)	1	4.45	C	4.65	4.40	A	D+	2.8	6.0	95.0
M. N.	(−)	1	4.62	D	4.70	4.60	C	C	2.0	8.0	80.0
M. IV	(+)	5	4.86	C+	4.12	5.48	B+	C−	11.0	7.0	91.2
M. IV	(−)	5	4.90	D+	4.18	5.46	B−	C	8.0	9.0	91.2
M. V.	(+)	1	5.80	B	4.25	6.30	B	C+	8.2	8.0	..
M. V.	(−)	1	5.75	D	4.40	6.20	C	B−	3.2	10.0	..
VII	(+)	1	5.48	B	3.50	5.52	C	B	13.8	4.0	88.0
VII	(−)	1	5.40	D	3.58	5.50	A	C+	10.7	5.0	84.0
Total	(+)	26	5.33	B−	3.98	5.79	B	C	10.7	6.2	88.7
	(−)	29	5.36	D+	4.05	5.74	C+	C−	8.4	7.2	81.3

studied were in various stages of development. Tests with 23 pairs of gametes of Phycomyces showed that in 20 cases the higher pH value was given by the larger convex gamete which contained more of a yellow substance (fat ?) and in which plasmolysis started later. Other observations showed that gametes with more yellow substance are always much stronger reducers of tellurium salts. A total of 56 races (in 13 species and 7 genera) of heterothallic Mucors and 7 races (in 5 species and 4 genera) of homo-

thallic species were tested in regard to fat and oxidase reaction with α-naphthol + dimethyl-*p*-phenylene-diamine and with indophenol, in vitro. (Zweibaum's method.) In every case a strong difference was shown in quantity of fat in the opposed gametes. Those with the larger amount of fat gave a higher pH value and showed the beginnings of plasmolysis later. Tests of gametes were made for other substances such as volutin, glycogen, etc., but as yet no constant difference has been discovered which can be directly related to the sex of the races from which the gametes are produced. Tests are being continued of other biochemical products and processes in Mucors that may show a difference between the two sexes.

If the biochemical behavior of Mucors be compared with that of higher plants and animals (cf. next paper) it will be noted that the (+) sex reacts in a similar way to females and the (−) sex to males.

The present investigation in connection with our previous study of the tellurium reaction[4] demonstrates: (1) that races of Mucors differ from one another biochemically, even when of the same sex; (2) that the (+) and (−) races show significant average biochemical differences in respect to (*a*) the factors involved in the Manoilov reaction, (*b*) catalase content, (*c*) reduction of $KMnO_4$ by extracts, (*d*) reduction of tellurium salts in living cells; (3) that sexual differences are suggested in regard to (*a*) peroxidase content and (*b*) total acidity of extracts; (4) that no sexual differences are evident in regard to pH in water or alcoholic extracts or to pH in medium on which the fungi have grown and in regard to certain other macro and microchemical tests; (5) that in their biochemical reactions, the (+) sex of Mucors corresponds to the female and that the (−) sex corresponds to the male of higher animals and plants discussed in the succeeding paper.

[1] Part of paper presented before the Physiol. Sect. of the Bot. Soc. of America, December 31, 1925. This investigation was carried on under a grant from the Committee of the National Research Council for Research on Sex Problems for whose support the authors gratefully acknowledge their indebtedness.

[2] Blakeslee and Gortner. See C. B. Davenport, "The Dept. Expt. Evol.," *Year Book Carn. Inst. Wash.*, **12**, 99 (1913).

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BIOCHEMICAL DIFFERENCES BETWEEN SEXES IN GREEN PLANTS[1]

BY SOPHIA SATINA AND A. F. BLAKESLEE

STATION FOR EXPERIMENTAL EVOLUTION, COLD SPRING HARBOR, N. Y.

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The preceding paper is the second in a series on the biochemical differences between the sexes in Mucors. The present article gives the preliminary results of a biochemical study of differences between the sexes in green plants. The technique employed is similar to that used with the Mucors except that green leaf tissue was used in place of the fungous mycelium and, except for the alcoholic extracts, the material was ground with sand.

Table 1 shows some of the tests with leaves of male and female plants of Rhamnus. The plants of this, as of other species, have been tested in pairs. There were six pairs, but, since the female in pair V was also used as the female in pair VI, only 11 individuals of the species were tested.

TABLE 1

BIOCHEMICAL TESTS WITH RHAMNUS CATHARTICA

PAIR NO.		I	II	III	IV	V	VI	STRONGER REACTION	WEAKER REACTION	AVERAGE
Color of extract	♀	yl	yl	yl	y gr	yl	yl	5	1	B−
	♂	gr	gr	gr	v y	p gr	gr	1	5	C−
Oxigenase	♀	C	O	C	O	D	D	4	0	C−
(3 reagents)	♂	D	O	D	O	O	O	0	4	D−
Peroxidase	♀	A	A	A	A	D	D	4	2	B
(3 reagents)	♂	B	D	B	B	A	B	2	4	B−
Tyrosinase	♀	..	..	..	D	..	..	0	1	D
	♂	..	..	..	C	..	..	1	0	C
Reduction	♀	5	4	..	3	4	4	5	0	4.0
($KMnO_4$)	♂	7	5	..	4	6	6	0	5	5.6
Reduction	♀	C	..	..	C	B	B	4	0	C+
(Na_2SeO_3)	♂	D	..	..	D	D	D	0	4	D
Reduction	♀	gr	..	..	gr	gr	gr	3	1	B
(Methyl. blue)	♂	bl	..	..	v gr	bl	p bl	1	3	C
Total Acidity	♀	4	4	4	5	4	4	5	1	4.2
	♂	3	3	3	6	2	3	1	5	3.3
pH of extract	♀	6.00	6.20	6.10	6.20	6.20	6.20	5	1	6.18
	♂	6.20	6.25	6.15	6.15	6.30	6.25	1	5	6.21
Tannins ($FeSO_4$)	♀	C	C	C	D	B	B	4	1	C
	♂	D	D	C	B	D	D	1	4	C−
Manoilov's	♀	A	B	B	C	A	A	5	1	B
reaction	♂	C	C	C	A	D	D	1	5	C

Color of Extract.—Extracts of leaves in 60 per cent alcohol usually show different colors for the two sexes. The extract from females is predomi-

nately yellowish while that from males is predominately greenish. All the females of the Rhamnus pairs gave yellowish extracts, although the female of pair IV was yellowish green and approached the male color. All the males in the series gave distinctly greenish extracts except the male of IV which was very yellow. The male of V was pale green but the color would place it with the other males.

Oxigenase.—The 3 reagents used were: (1) α-naphthol and dimethyl-*p*-phenylene-diamine, (2) alcoholic solution of gum guaiac, (3) α-naphthol. The reactions of all three reagents were similar but (1) was the strongest and (3) the weakest. It will be observed that in all cases tested the reaction of oxigenase is stronger in female leaves. In those plants in which no oxigenase could be detected, undetermined substances may have acted as inhibitors of the reaction. It should be borne in mind that in this as in other reactions, we may be indirectly testing inhibitors as well as testing the enzymes in the plants investigated.

Peroxidase.—The reagents used in the test for peroxidase were the same as those used for oxigenase with the addition of H_2O_2. The reaction of reagent (1) was usually too strong to show a differentiation between races, hence the weaker reaction of (3) was chiefly used in the tabulations. In 4 out of the 6 pairs the peroxidase reaction was stronger with the extract of females.

Tyrosinase.—In only one pair of the series was it possible to apply the test for tyrosinase before the leaves became unusable on account of the lateness of the season. In making the test, we followed the suggestion in paper of Minenkov[2] on chemical identification of sex. As reagent we used a solution of 0.05% tyrosin plus 0.04% Na_2CO_3. The females have shown a stronger tyrosinase reaction in Cannabis (2 pairs) and Humulus (1 pair), hence in pair IV the reaction may be considered a reversal.

Reduction of $KMnO_4$ was tested as with Mucors. In all the pairs tested the reduction was stronger in the females.

Reduction of Na_2SeO_3 was tested by method of Schreiner and Sullivan.[3] To 4 cc. of extract was added 2 cc. of the selenium salt plus 1 drop of 40% HCl and the resulting red precipitate roughly graded. By this test also, the females were the stronger reducers.

Reduction of Methylene Blue.—In making this test, a few drops of the reagent were added to the extract and the resulting color graded as blue, pale blue, green, or very green. Again, it will be seen that the females are the stronger reducers.

Total acidity was determined roughly by titration as was done with Mucors. The figures in this as in table 3 indicate the number of drops of $N/10$ KOH necessary to bring the extracts to the same grade of color with phenolphthalein as indicator. The numbers are comparable within any single species but cannot be depended upon to give the relative acidity

of different species. In all pairs, except IV, the extracts from females were the more acid.

The pH of extracts was determined colorimetrically. Slightly lower pH values were found for females, but, as in other species, there were no significant differences apparent.

Tannins were tested by 0.1% aqueous solution of $FeSO_4$ and the amounts of color roughly graded. In all pairs, except III and IV, the females showed the greater amount of tannins.

Manoilov Reaction.—In all pairs except IV, a correct identification of the sex was obtained by this method.

Except for pair IV which shows several reversals, there is considerable consistency in the results of the tests shown in table 1. On the average the females are superior in the oxidase and reduction reactions, in tannins and in total acidity, have a yellowish alcoholic extract and respond typically to the Manoilov reaction. In many tests, pair IV gave reversed

TABLE 2

IDENTIFICATION OF SEX IN GREEN PLANTS BY MANOILOV'S REACTION

SPECIES	NO. CASES	♀	♂	♂ BUT CHIEFLY ♀ OR ♂	CORRECT IDENTIFICATION	INCORRECT IDENTIFICATION
Salix discolor	2	1	1	..	2	.
Salix Babylonica	4	2	2	..	3	1 ♂
Salix sp.	4	2	2	..	4	.
Populus balsamifera	2	1	1	..	2	.
P. grand. × P. tremuloides	11	3	8	..	9	2 ♂
Sassafras	4	2	2	..	4	.
Myrica carolinensis	16	8	8	..	15	1 ♂
Rhamnus cathartica	11	5	6	..	10	1 ♂
Ailanthus glandulosa	7	2	5	..	5	1 ♀, 1 ♂
Morus (Teas' weep. × M. alba)	76	43	19	14	69	1 ♀, 3 ♂, 3 ♀
Cannabis sativa	6	3	3	..	6	.
Rumex acetosella	6	3	3	..	6	.
Rumex sp.	2	..	..	2	2	.
Arisaema triphyllum	2	1	1	..	2	.
Melandrium album	4	2	2	..	4	.
Rhus copalina	2	1	1	..	2	.
Rhus glabra	9	4	3	2	9	.
Humulus lupulus	2	1	1	..	2	.
Marchantia	2	1	1	..	2	.
Total	172	85	69	18	158	14

91.9% correct identifications; 8.1% incorrect identifications.

dreactions. Female individuals of Rhamnus produce fruit in great abundance and it was from their fruiting condition that the sex of the individuals was primarily determined. Since the tests were made while the fruit was still on the plants, it should be kept in mind that one may be dealing with conditions associated with fruit production as well as with sex.

The Manoilov Reaction has been tried in 172 cases included in 19 species and 14 genera as shown in table 2. In a number of cases (e.g., the F_1 of cross between erect and weeping mulberries) an individual bore flowers of both sexes with some branches predominately male and others predominately female, which usually gave a reaction corresponding to the sex expression. Out of 172 cases tested, there were only 14 reversed reactions making somewhat over 90% correct identifications which is essentially the same percentage obtained by us with Mucors and also with human blood tested by Manoilov.[4]

The reaction we have found an extremely delicate one, necessitating extreme care to ensure that the materials tested are strictly comparable. The proper proportions of the different reagents must be determined for each species. The color changes in a given pair of extracts treated at the same time differentiate the sex of the plants in question; females remain colored while males are decolorized. One pair of extracts cannot well be closely compared with another. To render results comparable, 5 to 10 gms. of leaves of similar age were used in making the paired extracts. The age of the leaves is a matter of importance. Thus the lower leaves of a male plant of Cannabis gave a "female" reaction when tested in comparison with the upper leaves from the same plant. The reverse condition was true for upper and lower leaves of a female plant of the same species. The upper, in comparison with the lower leaves, of a large plant of Rumex species gave a female reaction. The midrib of a mature leaf of this same plant gave a male reaction in comparison with the blade from the same leaf.

Sexual organs of flowers gave a reaction corresponding to the sex expression. Thus the stamens (or the whole male flower) gave male reactions and the pistils (or female flowers) gave female reactions in the following: 34 plants in 5 dioecious species, 27 plants in 8 monoecious species and 2 plants in 2 hermaphroditic species. Since the male obviously contained less sap than the female organs, it is possible that the reactions obtained were due primarily to quantitative differences in the extracts tested. The young ear of corn gave a male reaction in comparison with the young male flowers but the former appeared to have a more dilute extract.

The extracts after heating to boiling for 5 minutes, or after autoclaving up to 20 pounds' pressure, gave diminished reactions and their color changes were slower in appearance. An extract in 60% alcohol was found to give the best results. The use of 95 or 50% alcohol, as also pure water, generally spoiled the reaction.

The length of time of extracting was of importance and differed for different species. Two to 3 hours was found best for most of the Mucors and green plants, although for Rhizopus 24 hours was best. The filtered extracts of green plants in closed tubes were usable after several weeks.

For a pair each of 3 species of Mucors (Rhizopus, Phycomyces, Absidia glauca) which showed good Manoilov reactions, the extracts were buffered so that the pH of the (+) was lowered to about 3 and that of the (−) raised to about 8 and vice versa, but the reactions were not materially altered.

Table 3 gives a summary of some of the tests made with green plants. The male and female individuals show apparently significant average differences when tested for color of extract, oxigenase, peroxidase and total acidity and respond well to the Manoilov reaction. The differences in pH are apparently not significant.

TABLE 3

SUMMARY OF REACTIONS IN GREEN PLANTS

SPECIES	TOTAL RACES		MANOIL. REACT.		COLOR EXTR.		OXIG.		PEROX.		pH		TOTAL ACIDITY	
	♀	♂	♀	♂	♀	♂	♀	♂	♀	♂	♀	♂	♀	♂
Rhamnus	5	6	B	C	B−	C−	C−	D−	B	B−	6.18	6.21	4.2	3.3
Morus	9	9	B−	C	C+	C−	..	..	..	..	4.60	4.65	9.0	7.0
Ailanthus	1	1	C	D	C	D	C	D	B	C	4.4	4.8	7.0	5.0
Rh. copal.	2	2	C	D	C+	D	O	O	O	O	4.2	4.25	8.0	6.0
Rh. glabra	2	2	B	C	C+	C−	O	O	O	O	4.22	4.07	..	..
Populus hyb.	1	1	B−	D	D	C−	A	B	A	B+	6.0	5.8	4.0	6.0
Myrica[5]	6	5	C+	C+	C−	C−	O	O	B	C	4.47	4.51	..	..
Melandrium	2	2	C	D	C+	C−	C	D	A	B	..	..	..	..
Rhumex	3	3	C+	D	A	D	..	..	..	..	4.0	4.5	6.0	4.0
Humulus	1	1	C+	C	B	C	B	O	A	B	5.2	5.15	..	..
Cannabis	2	2	C+	D	B	D	B	C	A	B+	5.2	5.15	3.0	5.0
Total	34	34	C+	D+	C+	D+	C−	D−	B+	C+	4.85	4.90	5.9	5.2

It should be pointed out that all these biochemical differences between the two sexes so far discovered are akin to the sexual differences in regard to weight in the human species. While on the average the human male is the heavier and the female of the species the lighter, still if one should pick a pair of human individuals at random one might happen to capture an especially buxom female or an unusually meager male and reach, therefore, an erroneous conclusion as to the weight relations of men and women. It is due perhaps to non-sexual factors in respect to which individuals differ that there has been found as yet no simple and direct relation between the biochemical properties of a given individual and its sex, in the same way in which there has been found no simple and direct relation between the weight of a man or woman and sex. Our work has demonstrated the absolute necessity of basing any conclusion which may be drawn in regard to sex differences upon the behavior of a relatively large number of individuals.

It is true that in all cases the leaves were examined during the fruiting period or at time of flowering. Another season it will be possible to in-

vestigate the plants before flowering, but it is not believed that the differences found are due entirely to the fact that the females are changed in nutritive condition by the production of fruit. The production of embryos can have no relation, however, to the parallel results obtained with the Mucors in which sexual reproduction was prevented in the plants investigated.

The data presented we believe show more or less striking average differences in green plants between the sexes in respect to the Manoilov reaction, the color of leaf extracts, the presence of oxigenase, peroxigenase and total acidity.

Further parallel tests may give us a more complete biochemical picture of cell products and cell processes and enable us to distinguish those primarily associated with male and female protoplasm from individual non-sexual peculiarities.

[1] Part of paper presented before the Physiol. Sect. of the Bot. Soc. of America, Dec. 31, 1925. The investigation was carried on under a grant from the Committee of the National Research Council for Research on Sex Problems to whom the authors gratefully acknowledge their indebtedness.

[2] Minenkov A., *Naoutc. Agr. Journ.* (*Moscow*), **1**, 29–47 (1924).

[3] Schreiner O., and Sullivan M., *Science*, **31**, 310–311 (1916).

[4] Manoilov, E., *Münch. Med. Wochenschr.*, **51**, 1784–1789 (1924).

[5] The apparent equality of this species in respect to the Manoilov reaction is probably due to the fact that, in this as in other species listed in table 3, those individuals were included which were earlier listed as reversals in table 2.

THE MUCOR PARASITE PARASITELLA IN RELATION TO SEX[1]

BY SOPHIA SATINA AND A. F. BLAKESLEE

STATION FOR EXPERIMENTAL EVOLUTION, COLD SPRING HARBOR, N. Y.

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Parasitella simplex is a member of the group of fungi known as Mucors. It is commonly parasitic on other Mucors although it may be grown as a saprophyte. As a parasite it produces galls, which, when mature, resemble zygospores with curious outgrowths. The early stages are like those in conjugation or in the reaction known as imperfect hybridization.

It was from the resemblance of gall formation to conjugation and from the apparent sex-limited relation between Parasitella and host, discovered in the course of his brilliant investigations of sex and parasitism among Mucors, that Burgeff[2] was led to believe that parasitism had developed by way of an imperfect sexual reaction. Lacking a true imperfect hybridization between the sexual races of Parasitella and known (+) and (−) races of other Mucors, there was no method of knowing which sex of the

parasite was (+) and which (−). The terms (+) and (−), it may be mentioned, have been used to designate the opposite sexes in Mucors in which morphological differences between the two sexes did not allow the use of the terms male and female. With certain species, like Rhizopus, Burgeff found that both sexes of Parasitella formed galls with both sexes of the host. With Absidia glauca and A. caerulea, however, what he was led to call the (+) race of Parasitella formed galls only with the (−) sex of the host and what he called the (−) race of Parasitella formed them only with the (+) sex.

Our problem was to test this hypothesis of Burgeff and to discover reliable methods, if possible, of determining which sex of Parasitella is (+) and which (−). For convenience of discussion we may use the terms (+) and (−) for the same sexes of Parasitella that apparently were so designated by Burgeff. We can confirm in the main the curious cytological behavior in gall formation which he found. Without going into details, we may say that the cell content of host and parasite become mixed in the formation of a gall cell with basal outgrowths which is subtended by a thick-walled storage cell. Burgeff found no open connection in his material between the gall and the storage cell, but in our material we find stages which indicate that the intervening wall becomes dissolved and that nuclei enter the storage cell from the gall. When grown on certain Mucors as hosts, Parasitella forms only imperfect galls in which there is no mixture of cell contents of host and parasite nor development of storage cells nor of outgrowths.

Our investigations have to do with 4 races of Parasitella, 3 which for convenience of discussion we will call (−) and one (+). Morphologically they are similar, though differing somewhat in heights of growth. Contrary to the experience of other investigators, we find that when grown together saprophitically, the opposite sexes of Parasitella form numerous zygospores and also a certain number of perfect galls. We have found formation of perfect galls to take place in certain combinations between races of Parasitella belonging to the same sex, when no other Mucors were present. This, we believe, is a matter of some significance, although the galls were small and not numerous.

Each race of Parasitella was contrasted with 54 Mucor races (in 9 genera and 17 species). These selected host Mucors belong to both homothallic and heterothallic forms. The latter contained neutral races and weakest as well as strongest (+) and (−) races.

Table 1 shows the results of contrasts with 8 Mucor species of high sexual strength. In this and the other tables, perfect reactions are shown by capital letters—formation of imperfect galls by small letters. The strengths of reaction are indicated by the grades A to D. As may be seen, there is no difference in the kind of reaction in regard to the sexes of the parasite and

hose. Parasitella I, II and III, belonging to one sex, and Parasitella IV to the opposite sex, all give an A reaction with 3 pairs of races, imperfect galls with 3 other races—with a single exception which was a "0" and no reaction with 2 pairs, irrespective of the sex. A slight difference can be noted only in strengths of the imperfect reaction.

TABLE 1

GALL FORMATION BETWEEN OPPOSITE SEXES OF PARASITELLA AND (+) AND (−) SEXES OF OTHER MUCORS (HELICOSTYLUM, CIRCINELLA SPINOSA, ABSIDIA REPENS, SYNCEPHALASTRUM, MUCOR MUCEDO, MUCOR V, RHIZOPUS NIGRICANS, CHAETOCLADIUM BREFELDII[5])

(+) RACES								PARASITELLA	(−) RACES							
HELIC.	C. SPN.	A. REP.	SYNC.	M. MUC.	M. V.	RHIZ.	CHAET.	(−) ? RACES	CHAET.	RHIZ.	M. V.	M. MUC.	A. REP.	HELIC.	C. SPN.	SYNC.
0	0	0	0	0	A	A	A	P. I	A	A	A	0	0	0	0	0
0	0	c	b	a	.	.	.		.	.	.	a	c	d	0	0
0	0	0	0	0	A	A	A	P. II	A	A	A	0	0	0	0	0
0	0	c	b	a	.	.	.		.	.	.	a	c	d	0	0
0	0	0	0	0	A	A	A	P. III	A	A	A	0	0	0	0	0
0	0	c	b	a	.	.	.		.	.	.	a	d	0	0	0
								(+) ? RACE								
0	0	0	0	0	A	A	A	P. IV	A	A	A	0	0	0	0	0
0	0	d	b	a	.	.	.		.	.	.	a	b	b	0	0

There also was no difference in the kind of reaction in regard to the sexual races of Parasitella, when contrasts were made with 2 homothallic species and 5 neutral races[3] not shown in the table.

Particular attention was given to the contrasts with Absidia glauca and A. caerulea, the 2 species which, according to Burgeff's observations, have a sex-limited relation in regard to parasites. In all, 30 races were used, 21 races of A. caerulea and 9 races of A. glauca. Table 2 shows that

TABLE 2

GALL FORMATION BETWEEN OPPOSITE SEXES OF PARASITELLA AND (+) AND (−) SEXES OF ABSIDIA CAERULEA. (PERFECT REACTIONS SHOWN BY CAPITAL LETTERS, IMPERFECT REACTIONS BY SMALL LETTERS)

ABSIDIA CAERULEA NEUTRAL RACES					(+) RACES				PARASITELLA (−) ? RACES	ABSIDIA CAERULEA (−) RACES									
437	443	440	441	436	911	913	536	537		442	914	535	434	532	533	534	445	435	444	531	439
0	0	0	0	0	0	0	0	A	P. I	0	0	0	0	0	0	0	0	0	0	0	0
0	d	0	c	b	b	b	a	.		b	c	d	c	d	b	0	d	0	0	d	c
0	0	0	0	0	0	0	0	A	P. II	D	0	0	0	0	0	0	0	0	0	0	0
0	d	c	c	b	b	a	a	.		b	b	c	b	c	b	c	d	c	c	c	c
0	0	0	0	0	0	0	0	A	P. III	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	c	d	a	.		0	d	0	0	0	0	0	d	0	0	0	c
									(+) ? RACE												
0	0	0	0	0	0	0	0	0	P. IV	B	B	D	0	0	0	0	0	0	0	0	0
d	d	c	b	c	d	c	0	d		.	.	a	a	a	a	a	b	b	b	b	c

Parasitella IV (a (+) race by Burgeff's test) has a certain tendency to react more with the (−) races of A. caerulea; and the (−) race of Parasitella I, II and III—more with the (+) races of A. caerulea. This tendency is not an absolute one, since, out of the 4 Absidia (+) races, it is only one which develops perfect galls with the 3 (−) Parasitellas, and out of the 12 (−) races of the Absidia, only 3 which form galls with the (+) Parasitella. Moreover, one of these 3 (−) races (442) develops galls with Parasitella II, also a (−) by assumption.

If we consider the imperfect gall formation, the table shows that it is only the (−) Parasitella III which shows in fact any definite tendency not to react with the (−) races of Absidia and which fails entirely to react with the neutral races of this species. Furthermore, the other (+) and (−) races of Parasitella develop imperfect galls with nearly all the 21 Absidias, whether the latter are (+), (−) or neutral.

Table 3 shows the result of contrasts with Absidia glauca. It may be seen that the tendency of the (+) Parasitella IV to react perferentially with the (−) races of Absidia appears even weaker than in the previous case. The (+) Parasitella IV forms galls with 3 races only out of the 5 (−) Absidias while the same race of the parasite develops perfect galls with 2 (+) races of Absidia. A similar condition will be noted concerning the (−) Parasitellas I and II. They show a certain tendency toward preferential reaction with the (+) Absidia races, although they do not develop galls with one of them (915), and do form galls with a race of the same (−) sex (669).

TABLE 3

GALL FORMATION BETWEEN OPPOSITE SEXES OF PARASITELLA AND (+) AND (−) RACES OF ABSIDIA GLAUCA. (PERFECT REACTIONS SHOWN BY CAPITAL LETTERS, IMPERFECT REACTIONS BY SMALL LETTERS)

ABSIDIA GLAUCA (+) RACES				PARASITELLA (−) ? RACES	ABSIDIA GLAUCA (−) RACES				
915	917	667	668		669	666	919	918	920
0	B	B	B	P. I	C	0	0	0	0
b	.	.	.		.	d	0	0	0
0	B	B	B	P. II	B	0	0	0	0
b	.	.	.		.	d	0	0	0
0	B	C	B	P. III	0	0	0	0	0
c	.	.	.		0	d	0	0	0
				(+) ? RACE					
0	0	C	C	P. IV	B	B	B	0	0
c	0	.	.		.	.	.	b	c

If we consider the total reactions with the 2 species of Absidia, there are 2 facts which appear of significance: (1) the lack of gall reactions between races of Parasitella and the majority of the races of the sex toward which the parasite shows a certain tendency—in other words, between (+)

Parasitella and (−) Absidia and vice versa; (2) the definite gall reaction between races of Parasitella and races of the same sex of the Absidias.

Burgeff based his conclusions upon a single pair of races each of Parasitella and of the 2 Absidia species. The results we have obtained, however, with a larger number of races of Parasitella and of Absidia, emphasize the necessity of basing conclusions in regard to the relation between host and parasite upon a large number of individual races. The fact that gall formation can take place between both sexes of Parasitella and selected races of both sexes of the Absidias and the fact that gall formation fails to take place between both sexes of Parasitella and certain (+) and (−) races of Absidias, added to the fact that gall formation does occur between races of the same and opposite sexes of Parasitella, indicate that one is not dealing with a truly sex-limited relation between parasite and host.

It cannot be denied, however, that a tendency does actually seem to exist for one sex of the parasite to react preferentially with a single sex of the host in the two species of Absidia. The significance of this evident tendency cannot as yet be explained, although it may conceivably be related to predominant biochemical differences between the sexes, which we have demonstrated in other Mucors.[4] We applied to the Mucors some of the tests which we had used with male and female higher plants (cf. preceding papers, these PROCEEDINGS). It is interesting to note that the (+) Mucor races correspond in biochemical behavior to the females of higher plants and the (−) Mucor races correspond to males. It is perhaps significant that Parasitella IV, which showed a preferential tendency to form galls with (−) Absidias and should be ranked according to Burgeff with the (+) races, gave the characteristic female reactions with the tests used with this race, while the Parasitellas I, II and III, which according to Burgeff should be called (−), correspond in biochemical behavior to male plants.

From their biochemical behavior, therefore, with the possible additional evidence from gall reactions, which are doubtless biochemical in nature, we may provisionally assign the terms (+) and (−) to the sexual races of Parasitella.

[1] Paper presented before the Mycological Section of the Botanical Society of America, December 31, 1925. The experimental part of the work on gall reactions was completed in 1923. The biochemical tests with Parasitella cited from a previous paper in these PROCEEDINGS were made while working under a grant from the Committee of the National Research Council for Research on Sex Problems.

[2] Burgeff, H., *Botan. Abhandl.*, **4**, 1–135 (1924).

[3] Homothallic species: Zygorhynchus heterogamus, Mucor genevensis (2 races). Heterothallic species: Mucor spinosus, M. Rouxianus, Mucor sp., Pilaira, Mortierella sp.

[4] Satina, S., and Blakeslee, A. F., these PROCEEDINGS, **11**, 528–534 (1925).

[5] We have not yet determined the sex of the races of Chaetocladium by imperfect reactions but the gall formation with Parasitella is the same for each sex. When either

sex of Chaetocladium was grown with either sex of Parasitella, both species acted as host to the other parasite and galls were produced characteristic of both Parasitella and Chaetocladium. The parasitic behavior of Chaetocladium has been described in detail by Burgeff.[3]

THE PHYSIOLOGICAL PRINCIPLE OF MINIMUM WORK. I. THE VASCULAR SYSTEM AND THE COST OF BLOOD VOLUME

BY CECIL D. MURRAY

DEPARTMENT OF BIOLOGY, BRYN MAWR COLLEGE

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Introduction.—Physiological organization, like gravitation, is a "stubborn fact," and it is one task of theoretical physiology to find quantitative laws which describe organization in its various aspects. Just as the laws of thermodynamics were known before the kinetic theory of gases was developed, so it is not impossible that some quantitative generalizations may be arrived at in physiology which are independent of the discrete mechanisms in living things, but which apply to organic systems considered statistically. One such generalization is the principle of the maintenance of steady states—a principle which furnishes definite equations (of the type indicating equality of intake and output of elementary substances) applicable to the hypothetical normal individual. The purpose of these studies is to discuss the possible application of a second principle, the principle of minimum work, to problems concerning the operation of physiological systems.

The concept of adaptation has been treated in a quantitative manner by experimental morphologists, students of growth and form, who have shown again and again the tendency toward perfect fitness between structure and function in all sorts of plants and animals. Only rarely, however, has the concept of fitness been used as a *premise* for physiological deductions. The beginnings of theoretical or deductive physiology are to be found in the works of Galileo[1] and of Borelli,[2] who argued from the principle of similitude, as others have done since. Thompson's fascinating book[3] contains a wealth of material on this subject. Henderson's classic essay[4] covers the history of the teleological problem, and presents his own proof that the teleological aspect of nature (until Darwin's time associated with the minutiae of biological adaptations, and in the latter part of the last century associated with primitive theological doctrine) has its real roots in the properties of matter and in the laws of physics and chemistry. Thus it may be seen that organization is a legitimate field for scientific inquiry and not an "affair of the reflective judgment."

No one can escape the impression of a physiological determinism as exemplified by the narrowness of the "physiological range;" but the hypothesis of the constancy of the internal environment, being in effect a denial of adaptive change, holds out no hope whatever of interpreting quantitatively the phenomena of organization. Let us start then from the basis that organization and adaptation are observed facts, presumably conforming to definite laws because, statistically at least, there is some sort of uniformity or determinism in their appearances. And let us assume that the best quantitative statement embodying the concept of organizatin is a principle which states that the cost of operation of physiological systems tends to be a minimum, and that cost is to be measured in units, like the Calorie and the erg, which have dimensions equivalent to those of *work*.

The specific problems to be discussed all center around oxygen transport in man. Oxygen transport is the oldest and the most advanced field of quantitative physiological inquiry, and, therefore, it is the most suitable subject for theoretical studies. The functions which must be performed by the oxygen transport system, if a steady state is to be maintained, are relatively clear-cut, the factors involved in the efficiency of transport are discernible to a large extent, and there is little doubt that, through all the trials and errors of individual growth and evolution, an efficient mode of operation has been arrived at. (For physiological studies the main anatomical features may be taken as given in outline, and similarly properties of the red blood corpuscle, etc.) That the normal or average operation of oxygen transport *is* the most efficient or economical operation, will not be the special burden of the argument; but, by assuming this as a postulate generalized from observation, the analysis of the factors involved becomes less cumbersome. Moreover, the result at least contributes to a description of a theoretically efficient system with which the actual manner of operation may be compared, thus bringing to light discrepancies and new problems, and throwing into relief the exceptional and the truly pathological. The principle of economy is more fundamental than any particular conclusion based on fallible appreciation of the factors determining cost and function in any given case, but a large discrepancy, between the theoretical result and the actual normal operation, inevitably suggests an unknown factor to be searched for. The theoretical problem is essentially to find the best fit between criteria of cost and function, *and* the deductions from some precise quantitative statement of the general principle of economy. To evaluate certain general equations numerically, a table of "standard values" has been compiled, and the special tentative assumption is made that the basal state, represented by values given in the table, is a state at which all the factors to be discussed operate together most efficiently. Any modification of this assumption merely requires the sub-

stitution of different values in the equations, granting the latter to be applicable. We may now proceed to some specific problems.

The Vascular System and the Cost of Blood Volume.—If we examine the arterial system bearing in mind the question of economy, we find that there are two main antagonistic factors. If the vessels are too small, the work

TABLE OF "STANDARD" VALUES AND MISCELLANEOUS DATA

Values for factors representative of normal basal conditions, collected mostly from physiological texts, are given in brackets, following the definitions of the numbered symbols, these having been taken as the primary factors. Some values for derived factors (un-numbered) are included. Most of the definitions refer particularly to blood vessels considered, section by section, as cylindrical tubes of uniform radius. Units are in c.g.s. system, unless otherwise noted.

1. r = the radius [for capillaries, 3.5×10^{-4} cm.].
2. l = the length [for capillaries, 0.05 cm.]
   s = the surface area, $= 2\pi rl$.
   vol. = the volume $= l\pi r^2 = rs/2$.
3. u = the velocity of blood, e.g., of a blood corpuscle [for capillaries, 0.05 cm./sec.].
   n = the average number of capillaries through which blood is circulating at any instant.
   f = rate of blood flow in a vessel, i.e., the amount of flow in cubic centimeters per second.
4. nf = the total blood flow per second [for basal conditions in man, 83.3 cc./sec.]. In the text nf will not be used as a symbol—it will be clear from the context whether f refers to a single vessel or to the total flow.
5. η = the viscosity [for blood of average composition at 37°, 0.028].

From the above, we find: f, for a capillary, $= u\pi r^2 = 1.925 \times 10^{-8}$ cc./sec.; vol., for a capillary, $= 1.925 \times 10^{-8}$ cc.; and n vol., the total active capillary volume, $= nf$ vol./$f = 83.3$ cc.

Poisseuille's well-known equation for the flow of liquids in tubes is the following:

$$p = \frac{f \cdot l \cdot 8\eta}{\pi r^4}$$

where p is the difference in pressure, in dynes per square centimeter, between the two ends of the tube. Applied to capillary flow, using values given above, we find: $p = 4575$ dynes/cm.^{2} (or, dividing by 1333 to convert to mm. of Hg, $p = 3.43$ mm. Hg). When it was thought that in capillaries the fall in pressure was about 40 mm. Hg, it was the fashion to regard Poisseuille's equation as inapplicable to capillary flow. But the direct determinations cited by Krogh[6] are only a trifle higher than the value derived above. This recent work thus restores a much desired consistency in the subject of hemodynamics. In capillaries the pressure *gradient* is higher than elsewhere, but, the capillaries being very *short*, the loss in pressure in these is only a small fraction of the total blood pressure.

The work done in unit time against friction in a tube (neglecting eddies and intermittent acceleration attending pulsating flow) is given by the product pf. For the effective work (approximately) of the heart, taking $p = 174{,}000$ dynes /cm.^{2} (= 130 mm. Hg for the systemic blood pressure) we have: $pf = 1.45 \times 10^7$ ergs/sec. (or, multiplying by 2.065×10^{-6} we have: $pf = 30$ Cals./day).

For the total circulating blood volume, let us take the value 5000 cc., of which, it is estimated, 1500 cc. are in the arteries of the greater circulation.

required to drive the blood through them becomes too great; if the volume of the vessels is too large, the volume of blood, being equally large, becomes a burden to the whole body. The problem is therefore to determine whether there is a compromise which is more efficient than any other, and to study the interplay of the factors.

Poisseuille's equation (see reference table) for the law of flow in cylindrical tubes may be taken as a very fair approximation giving the relationships required. If both sides of the equation, as given in the table, are multiplied by f, the flow, one obtains the work, pf, in ergs per second, lost through friction—a function we may call simply the friction—for any uniform section of the arterial system. Thus:

$$pf = \frac{f^2 \cdot l \cdot 8\eta}{\pi r^4}. \qquad (1)$$

To study the antagonism between the friction and the volume of blood, the latter factor must be multiplied by a dimensional constant. Let b, then, be the cost of blood in ergs per second per cubic centimeter of whole blood of average composition (and let B be the cost in Calories per day per cc. of blood). There is, as far as I can see, nothing arbitrary about this step: it is certain that the maintenance of blood requires fuel. (The cost of blood may, however, be a complex account distributed among such factors as the small metabolism of blood itself, the cost of upkeep of all the constituents, perhaps especially of hemoglobin, the cost of the containing vessels, and the burden placed upon the body in general by the mere weight of blood.) The cost of blood, in ergs per sec. per cc., is then given, for any particular section of the arterial system, by the expression $b$vol., or $bl\pi r^2$. The total work, E, involved in operating a section of artery is then given by the equation

$$E = pf + b\text{vol.} = \frac{f^2 \cdot l \cdot 8\eta}{\pi r^4} + bl\pi r^2. \qquad (2)$$

Now the condition for maximum economy of work, given the flow, f, and the length, l, of some arterial section, is that the total work, E, shall be a minimum. We have then two variables, E, and the radius, r. Differentiating and equating to zero, we obtain:

$$\frac{dE}{dr} = -\frac{4f^2 \cdot l \cdot 8\eta}{\pi r^5} + 2bl\pi r = 0 \qquad (3)$$

and, therefore,

$$b = \frac{2f^2 \cdot 8\eta}{\pi^2 r^6}. \qquad (4)$$

According to the assumptions stated, equation 4 is the general equation which must be fulfilled for maximum economy of work in any section of

artery. It will be referred to again in other connections. For the present we will use it to make an estimate of the value of b as follows. From equations 1 and 4 we may derive the equation

$$pf = 0.5bl\pi r^2 = 0.5b\text{vol.} \qquad (5)$$

At maximum efficiency equation 5 holds for any and all parts of the arterial system, and also for the whole system. For the latter case the total effective work of the left ventricle, pf, may be estimated (neglecting work done in the intermittent acceleration of blood), and the volume of blood in the arterial system may be roughly estimated. Values from the table may be substituted, then, as follows:

$$b = \frac{2pf}{\text{vol.}} = \frac{2 \cdot 174 \cdot 10^3 \cdot 83.3}{1500} = 19{,}300 \text{ ergs/cc. sec., or}$$

$$B = 0.04 \text{ Cal./cc. day.}$$

This result may be interpreted as follows: were blood a cheaper material than is shown by the value obtained, one might expect all arteries to be uniformly larger than they are, thereby greatly reducing the burden on the heart. (For example, doubling the radii of all arteries, the lengths of which are constant, would mean a four-fold increase in volume, and a reduction of the work of the heart to one-sixteenth!) And conversely, if blood were a more expensive material we would be in danger of annihilation by a scant-blooded, large-hearted race. The result obtained, considered as a first approximation, rests upon the general concepts of evolution and physiological fitness. We may test the plausibility of the result by comparison with other tissues. Taking 2500 Calories per day as the basal energy expenditure of a man weighing 70 kg., the rate per gram is 0.036 Calorie. Compared with this value, the result 0.040 Calorie per cc. of blood appears plausible. But the cost of blood has been estimated by comparison with the mechanical work of the heart, an organ the efficiency of which is about 30 per cent. The "true" cost of blood should therefore be about 0.13 Cal. per day, or more nearly comparable to the energy requirements of the more active tissues of the body. The deduction from the principle of economy of operation of physiological systems is therefore not unreasonable.

From a consideration of the energy relations in the arterial system we may now turn to the capillaries. To begin with let us assume that the capillaries are subject to the same conditions as the arterial system. We may substitute directly in equation 4 the values for capillaries from the

standard set, since now we are dealing with a relatively homogeneous section of the vascular system. Thus we obtain:

$$b = \frac{2(1.925 \cdot 10^{-3})^2 \cdot 8(0.028)}{\pi^2 (3.5 \cdot 10^{-4})^6} = 9180 \text{ ergs/cc. sec., or}$$

$$B = 0.019 \text{ Cal./cc. day.}$$

We might, however, make an alternative assumption in this case, namely, that for an individual in a given state, the variables to be considered as determined (the factors to be kept constant in differentiating the equation) should be the flow, f, as before, and the *surface area*, s (instead of the length) of the capillary. Since $s = 2\pi rl$, and vol. $= rs/2$, we may write equation 2 in the form:

$$E = \frac{f^2 \cdot s \cdot 8\eta}{2\pi^2 r^5} + \frac{brs}{2}.$$

Differentiating as before, we obtain:

$$\frac{dE}{dr} = -\frac{5f^2 \cdot s \cdot 8\eta}{2\pi^2 r^6} + \frac{bs}{2} = 0, \text{ and } b = \frac{5f^2 \cdot 8\eta}{\pi^2 r^6}. \qquad (6)$$

Comparing equation 4 with equation 6, it is seen that the value of b determined by the latter will be 5/2 greater than the value obtained by the former. The alternative assumption leads to the result:

$$B = 0.019 \cdot 2.5 = 0.047 \text{ Cal./cc. day.}$$

The last assumption is perhaps theoretically preferable, and it leads to a closer agreement between the value of B as obtained from the observed relations in capillaries with the value obtained from estimates of relations existing in the arterial system as a whole. The approximate agreement, in either case, based on figures differing enormously in magnitude, strongly supports the reasoning involved in the application of the principle of minimum work. If we had, for example, used the first value obtained for b (19,300), and substituted this in equation 6, we could have made a fair estimate of the radius of a capillary or the flow of blood through it, one of the latter being known.

Many relations are contained in equations 4 and 6, and one of these may be appropriately mentioned here. If equation 4 is written in the forms:

$$f^2 = \frac{r^6 \pi^2 b}{16\eta} \qquad f = r^3 \sqrt{\frac{\pi^2 b}{16\eta}} \quad \text{or} \quad f = kr^3 \qquad (7)$$

we see one of the simplest requirements for maximum efficiency in the circulation—namely that the flow of blood past any section shall every-

where bear the same relation to the cube of the radius of the vessel at that point. In terms of velocity, since the velocity, u, is given by the relation $u = f/\pi r^2$, we have from equation 7 the requirement: $u = r\sqrt{\frac{b}{16\eta}} = k'r$, in words, that the velocity of blood is proportional to the radius of the vessel. We have already made three estimates of b: (1) from relations in the arterial system as a whole (19,300), (2) and (3) from relations in capillaries according to two possible assumptions (9180 and 22,950). A fourth estimate may be made from observations of the velocity of blood in a single artery. Tschuewsky[5] has determined the velocity of blood in, and the radius of, the carotid artery in dogs. Averaging five normal cases from page 270 of his paper, one finds: $r = 0.159$ cm., and $u = 25.5$ cm./sec. Assuming the "standard" viscosity, $b = (0.669\ u/r)^2 = 11{,}520$ ergs/cc. sec. The agreement, in order of magnitude, between these results is, I think, convincing evidence that the cost of blood volume is operative in determining conditions in the vascular system, from a capillary to an artery of a diameter at least five hundred times greater.

For larger arteries than those considered above, the simple equations no longer hold. Equation 1 only accounts for a small portion of the mechanical work required for the flow of blood in the *aorta*—most of the work required is to produce the intermittent acceleration of the blood at each heart beat, the lesser part to overcome friction. Values for b, derived from conditions prevailing in the aorta, would be much too small unless the total energy involved in the flow of blood were taken into account. This is the same as saying that the aorta, compared to the rest of the vascular system, seems to be disproportionately large—a fact which has long been recognized. From the standpoint of economy of work, the aorta is analogous to the large pipe which connects a pumping station with a reservoir—the function of the reservoir being performed by the elasticity of the aorta. The large pipe minimizes the high acceleration associated with intermittent flow, and the reservoir largely converts the intermittent into a continuous flow. The work required to overcome the inertia of blood is only significant when the velocity is high; hence, the larger the animal the larger must be the aorta in comparison to the rest of the vascular system and the normal blood flow of the animal.

The bearing of these results on the process of oxygen exchange in capillaries will be dealt with in a succeeding part.

To express here my gratitude to Professor Henderson, for much enlightenment shed upon confused questions time after time, is a genuine satisfaction. To Dr. F. H. Pike's early insistence that physiology is "a problem in maxima and minima" I owe the basic idea of this paper.

[1] Galilei, Galileo, *Dialogues Concerning Two New Sciences* (Leyden, 1638), Trans. Crew and de Salvio, Macmillan Co., 1914 (v. pp. 130–3 and 150).

[2] Borelli, G. A., *De motu animalium*, Rome, 1681.

[3] Thompson, D. W., "On Growth and Form," Camb. Univ. Press, 1917.

[4] Henderson, L. J., "The Order of Nature," Harvard Univ. Press, 2nd ed., 1925.

[5] Tschuewsky, J. A., *Pfluger's Arch.*, **97**, 1903 (210–288).

[6] Krogh, A., "The Anatomy and Physiology of the Capillaries," Yale Univ. Press, 1922.

Previous work on the economy of the circulation is to be found in the articles by W. R. Hess. (See especially, *Pfluger's Arch.*, **168**, 1917 (439–490). In this paper he deals with the compromise between resistance to flow and the volume of a vessel. He develops equations (which can be derived from those given in the present paper), but, failing to recognize the significance of his units, the dimensions of his constants, and particularly the fact that economy is a question of *work*, he misses what seems to be the essence of the problem. The fundamental equations given in the present paper cannot be derived from those of Hess.)

THE SIGNIFICANCE OF CHANGES IN THE ELECTRICAL RESISTANCE OF THE BODY DURING SLEEP

By Curt P. Richter

Psycho-Biological Laboratory, Henry Phipps Psychiatric Clinic, Johns Hopkins Hospital

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Our knowledge regarding the changes which take place in the body during sleep is still very limited. Like most other things common to our daily life, sleep has always, except on a few occasions, enjoyed almost complete immunity from experimental investigation, and at the same time it has been the topic of an almost endless number of theories and speculations. Some experiments on blood pressure, pulse rate, and respiration, and a few measurements of the intensity of sleep have been made. Of these the experiments on the intensity of sleep were most interesting and promising. The first investigations along this line were undertaken in 1863 by Kohlschütter,[1] a student of Fechner; and since then a few other investigators, Monninghoff and Piesbergen,[2] Michelson,[3] Howell,[4] have either repeated or slightly extended the original experiments. Depth of sleep was measured in terms of the intensity of acoustic stimulus necessary to awaken the subjects. The stimuli were repeated at short intervals and in progressively increasing intensities. The results of these experiments showed that the intensity or depth of sleep increases very quickly, reaches a maximum before the end of the second hour, and then decreases again equally rapidly to a low level at which it remains, with small fluctuations, until the end of the sleep period. This result is obviously not in agreement with general experience. It is a fact of common observation that

there are the widest individual differences in the depth of sleep at different times after the onset. Some individuals sleep just as soundly and are awakened with as great difficulty after eight as after two hours' sleep; some awaken easily at any time. A part of the fallacy of this experimental work must probably have been due to the fact that the subjects were constantly under a strain waiting to be awakened, and the sleep accordingly was never normal. It may be said that any experiments on the depth of sleep which require the awakening of the subject are very liable to similar errors and misinterpretation.

In the present work a different approach to this problem will be described, one which does not involve the interruption of sleep and all of the resulting complications. At the same time it will be shown how the quality of sleep, an aspect hitherto neglected, may also be measured and studied experimentally.

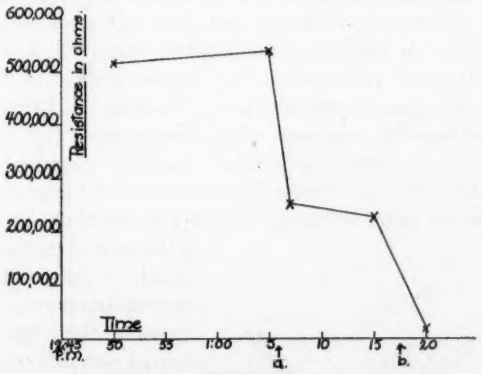

FIGURE 1

Our observation made several years ago that the electrical resistance offered by the body to a galvanic current is markedly increased during sleep (in one individual from 30,000 to 500,000 ohms), was the point of departure for the following experiments. Waller[5] had made a similar observation many years before. He found, while taking resistance records of the diurnal variation of the electrical resistance of his own body, that the resistance was very much higher in the morning just after waking than it was the night before. More recently Pieper[6] in Germany working on infants, and Chambers and Farmer[7] in England working on students, found a marked increase in resistance during sleep.

Our records were obtained by measuring the resistance offered to the passage of an imperceptible constant galvanic current usually from one hand to the other. Electrodes were especially devised for this purpose.[8] They were made of solid pieces of zinc covered with a thick paste made

by mixing kaolin with saturated zinc sulphate solution. These electrodes have the advantage that they are non-polarizable, that they make intimate contact with the skin without injuring or irritating it, and that they can be easily attached and removed, usually without interrupting sleep. The resistance was measured with a string galvanometer.

As a basis for an understanding of the results of our sleep experiments, it is necessary first to present the results of several experiments which show what factors are involved in the electrical resistance of the body. By means of a fairly simple experiment we were able to demonstrate conclusively that the resistance is localized almost entirely in the skin. It was found that a puncture through the skin with a hypodermic needle, even of the finest bore, reduces the resistance instantaneously from any level however high, practically to zero, as may be seen in the graph in figure 1. In this experiment the electrodes were attached to the back of each hand and the resistance offered to the passage of a current from one hand to the other was measured before and after the punctures were made. At the beginning the resistance was 540,000 ohms. A hole through the skin of the left hand, indicated at "*a*," caused a drop to 250,000 ohms; a hole in the right hand, indicated at "*b*," a drop to 15,000 ohms. This result was confirmed by numerous other observations.

With this fact definitely established, that the electrical resistance is localized in the skin, it became important to determine whether the porous area of the palm of the hand and the relatively non-porous area of the back of the hand contribute equally to the resistance. Other experiments showed that the resistances of these two parts of the skin are very different and respond differently to various physiological stimuli. These determinations were made by taking simultaneous readings of the resistance offered to the passage of a current from the palm of one hand to the palm of the other, and from the back of one hand to the back of the other. In the present connection it is sufficient to point out a few of the differences. Subcutaneous injections of atropin (1/100 to 1/50 grains) at a point distant from the electrodes, increase very markedly the resistance of the palms. The results are recorded in figure 2. Here resistance in ohms is given on the ordinates, and the time of day in hours on the

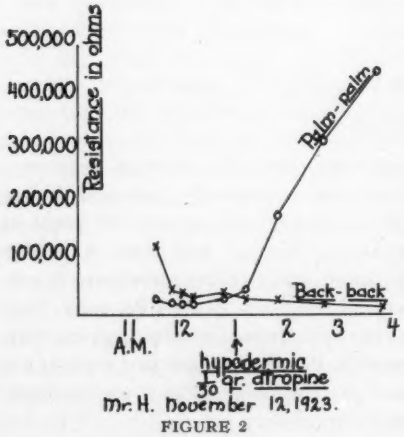

FIGURE 2

abscissae. Several readings were made between 11 A.M. and 1 P.M., before the atropin was injected. During this time the palm–palm resistance averaged about 20,000 ohms; the back–back resistance was gradually decreasing. After the injection the former increased steadily up to 460,000 ohms, while the latter continued to decrease at about the same rate as before, giving no evidence whatsoever of having been affected by the atropin. A similar result was obtained in a number of other individuals. Because of the well known paralytic action of atropin on the nerves of the sweat glands, the inference appears likely that the increase in resistance

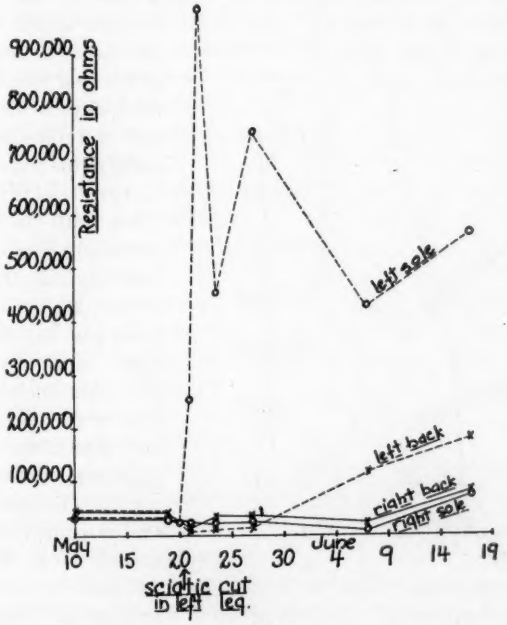

FIGURE 3

on the palmar surfaces, where we know that sudoriporous glands are extremely abundant, is due to the effect of atropin on these glands. However, we are forced to conclude further that the effect of the drug on the sweat glands of the back of the hand must be masked in some as yet unanalyzable way. The action on the back of the hand may eventually be explained by the determining rôle of structural arrangements other than sweat glands and different from those of the palmar surface.

A very similar result was obtained in monkeys by actually cutting the nerves to the hands and feet. In three monkeys the sciatic and anterior crural were sectioned. This operation was followed by an enormous in-

crease in the palm–palm resistance, without any change whatsoever in the back–back resistance, as may be seen in the record of one of the animals in figure 3. The resistance is given in ohms on the ordinates; the duration of the experiment is given in days on the abscissae. In this graph the resistances of the skin of the sole and back of the two feet are given separately. It will be seen that for the two days before the operation the resistance of all four areas was nearly the same. Then immediately following the section of the sciatic and anterior crural of the left leg, the resistance of the sole of the foot increased within three days to 990,000 ohms, and still retained approximately this high level of resistance after a month. These with the atropin experiments, demonstrate conclusively that the resistance of the palmar surface of the hand and foot is dependent upon and regulated by nervous impulses, while that of the dorsal surface is not dependent on nervous impulses. Although we do not know definitely just how the resistance of the non-porous areas is regulated, we have a considerable amount of evidence which suggests that it is dependent on the changes in the epithelial cells of the skin in agreement with the results of Ebbecke's[9] interesting experiments. Ebbecke showed that the skin, with its many cells, responds to stimulation with an increase in permeability, very much the same as the semi-permeable membrane of a single cell. Thermal, galvanic, mechanical and chemical stimuli bring about local changes in resistance.

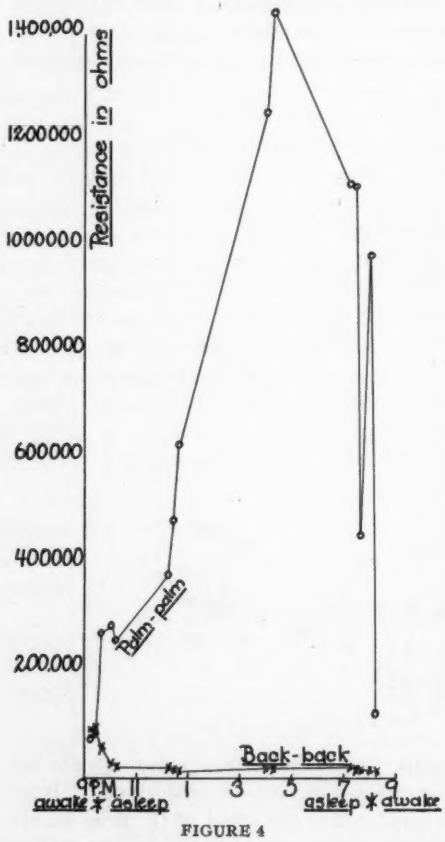

FIGURE 4

Previous workers, attaching one electrode over a porous and the other over a non-porous area of skin, or dipping the entire hand in salt solu-

tion, failed to make the distinction in the physiological function of the palm and back which has been brought out in the present work.

In the sleep experiments also, the first point to be established was that the backs and palms of the hands are affected very differently so far as changes in resistance are concerned, as is demonstrated in the graph in figure 4. Here the resistance is given on the ordinates in ohms, and the duration of the experiment in hours on the abscissae. There are two curves, one for the palm–palm, the other for the back–back resistance. The former shows a very marked increase during sleep, from 70,000 ohms to 1,450,000 ohms; the latter shows a slight decrease. In the sixteen individuals on whom sleep records have thus far been taken, we have found in all cases without exception the palm–palm record increased, usually quite markedly, while the back–back resistance increased in some, decreased in others. How do these changes in resistance correlate with other conditions present in the subjects?

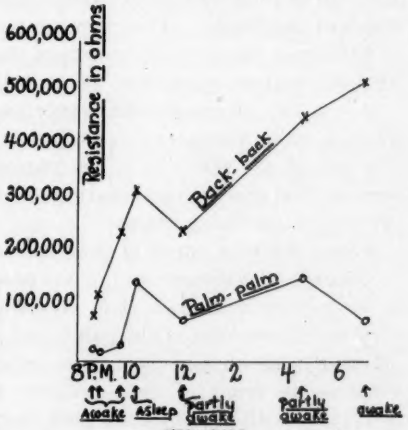

FIGURE 5

It was found that the changes in the resistance of the palms follow closely the depth or intensity of sleep. As soon as the individual drops off to sleep, the resistance begins to increase slowly in some, very rapidly in others. Those in whom it reaches a high level, as for instance, the patient whose record is shown in figure 4, sleep very heavily and can be aroused only with great difficulty. This patient did not show the least response to loud noises around the laboratory and seemed completely oblivious to having the electrodes attached and removed. In contrast to these individuals are those in whom the increase in palm–palm resistance is not so great. In the patient in figure 5, for example, the sleep is light, as is shown by the fact that he responded to even slight noises and tactual stimuli with changes in respiration, sighs, changing of position in bed, etc. It may be mentioned here that in most of these experiments the subjects were under continuous observation throughout the night so that all responses and activity could be noted.

This close correspondence between the depth of sleep and the resistance is shown further very clearly by the records of the following experiments. It was found that awakening, however suddenly brought about, is followed instantly by a drop of the resistance from any level to the waking level.

This can be seen in the graph in figure 4. At 8 A.M. the patient was deeply asleep, and his resistance was 980,000 ohms. Five minutes later he was awakened as suddenly as possible, and his resistance decreased to 120,000 ohms.

Several similar observations were made on a monkey which, while held in the lap of an assistant in a darkened room, slept fitfully. The resistance followed the change in sleep so closely that it was possible to state quite accurately, without seeing the animal at all, whether it was awake, drowsing or asleep, simply on the basis of the resistance readings.

This, then, offers a new method of measuring the depth of sleep and has the marked advantage that its successful use does not require the interruption of sleep. Because the individual variations are too great we are not able to give an average normal curve for the intensity of sleep. This can be done only with a much larger group of individuals and under standard conditions. The curve of the intensity of sleep is not nearly so uniform or simple as the results of the experiments of Kohlschütter and the later workers would lead one to believe.

It is a fact of considerable importance that sleep has the same effect on palm–palm resistance as paralysis or complete section of the nerves to this part of the skin. It is not known at present, however, whether in sleep we deal also with an interruption of the nervous impulses, or with the effect of an inhibitory process.

A very different aspect of sleep was illuminated by the investigation of the changes of resistance in the non-porous skin of the back of the hands. It was pointed out above that physiologically this skin differs very much from the porous skin of the palms and also that during sleep it responds differently, showing an increase in some individuals, a decrease in others. What is the origin of these contrary results? It was found that the individuals with an increase in back–back resistance during the night were able to relax more or less completely during sleep, and were refreshed in the morning. That those with a decrease were often obviously strained was shown by their gritting the teeth, talking, groaning, etc., activities possibly connected with dreaming. These individuals awakened in the morning feeling tired. The results suggested that we were dealing with two different kinds of sleep, a quiet, relaxed sleep, and a strained sleep connected with muscular activity. They are in agreement with the results obtained in other experiments carried on during the day on the relation between resistance and tenseness in different types of patients and normals. It was found that in early schizophrenics and normals who are usually obviously tense and strained, the back–back resistance is low, while in cases of stupor and normals who are obviously free from tenseness, the resistance is high.

Attention has recently been called in a very conclusive way to the dif-

ference between these two kinds of sleep by MacWilliam[10] in his work on the changes of blood pressure during sleep. Contrary to the result of previous investigators this work showed that sleep is not necessarily accompanied by a decrease in blood pressure, that often there is a marked increase. Thus he says: . . . ."there are two entirely different conditions in question in sleep—1, sound sleep with lowering of pressure; 2, disturbed sleep, dreaming, etc., which may be attended by remarkable elevations of pressure, e.g., systolic pressure raised from 125 to 182 mm., or from 130 to 200, etc.; diastolic pressure raised from 75 to 105 mm., etc. These changes were much greater than were induced in the same individuals by moderate exertion (cycling, walking, stair climbing, etc.), straining, abdominal efforts, dose of atropin to remove vagus control over the heart, mental excitement, etc. In view of the rapid development of such changes in sleep, especially in dreams of motor effort, nightmares, etc., it is evident that a formidable strain—harmless in the young and healthy person—may thus be thrown on the weak points of the circulatory system, whether these be cardiac with susceptibility to anginal attacks or to ventricular fibrillation and sudden death, or arterial with risk of hemorrhages, cerebral (especially in the recumbent posture), gastro-intestinal or pulmonary. The conception of sleep as a period of quiescence and recuperation has thus to be qualified by the contingency of disturbed sleep with active calls on the nervous system the heart and the blood vessels. The mechanism of the rise of pressure in disturbed sleep differs in some respects from that present in ordinary muscular exertion, since in the former the pumping action of working muscles, greatly augmenting the venous return to the heart, is absent. The above-mentioned disturbances may occur during disturbed sleep when there is after waking no recollection of definite dreaming."

This method of measuring the changes in resistance may throw some light also on the differences between normal sleep and certain pathological conditions which closely resemble sleep. We have had occasion to measure the resistance of a number of patients in catatonic stupors, some of which so closely resembled sleep that it was impossible to tell by looking at the patients that they were not asleep. They remained in the same position in their beds for hours at a time, without giving any sign of being in contact with their surroundings; they showed no responses to stimuli; generally they gave the impression of being completely relaxed and inert. It is an interesting fact that these stupors which so closely resembled sleep, should give such very different electrical resistance records. A typical record of one patient is shown in figure 6. This gives hourly readings of resistance throughout an entire day, during which time the individual seemed to be asleep. The palm–palm resistance, which we have shown invariably increases during normal sleep, remained on a flat low

level varying from 8000–13,000 ohms. This is even considerably below the average palm–palm resistance for normals (45,000 ohms) during the waking state. If we keep in mind the fact that the resistance of the palm is dependent on nervous stimulation, that it follows closely the dropping out of mental activity during sleep and its return on awakening, we may conclude that in these patients, the unusually low palm–palm resistance indicates an increased nervous activity, an amount even greater than is found in normals during the waking state. The back–back resistance on the contrary is very high, in some individuals as high as a million ohms. This result is in keeping with the results of the sleep experiments, where a high back–back resistance was also found to be associated with freedom from muscular strain and a generally relaxed condition. In these patients, then, we have evidence for heightened nervous activity and a diminished muscular activity. It would seem that the nervous activity somehow is not permitted to reach, or is blocked from reaching the muscles. We have good reason to believe, on the basis of clinical observation, that in this condition there is much nervous activity and that the individuals are in contact with what is going on, as is demonstrated by their ability after coming out of the stupor to recount in detail, with considerable accuracy, everything that happened around them during the stupor, and by the appearance of entirely new and widely elaborated phantasies.

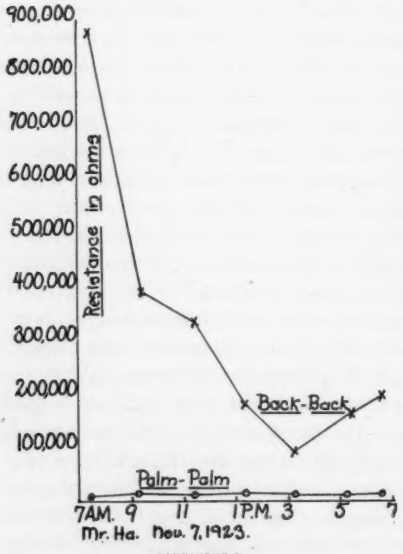

FIGURE 6

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